ELECTROCHEMICAL STUDIES IN OXIDE FORMATION ON SOME METALS.

by

GEORGE DREVER, B.Sc., (Edin.)

Thesis for the Degree of Doctor of Philosophy.

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Part I.

Anodic and cathodic behaviour of palladium, rhodium and iridium electrodes in dilute sulphuric acid and dilute sodium hydroxide.

Introduction

Metals can be classified into three broad groups according to their electrochemical behaviour.

(1) In the first group are found those metals which pass into solution as ions when they are made the anode in an electrolyte. This process takes place at or near the normal potential of the metal in the electrolyte and can be represented by the following simple scheme:

$$M = M^{+} + \epsilon$$

This process continues until all the metal has passed into solution. This group is typically represented by the anodic solution of copper in sulphuric acid.

(2) In the second group are found those metals whose behaviour on anodic polarization with low current densities is similar to that of metals in the first group, but which exhibit the phenomenon of passivity on treatment with larger current densities. Generally speaking, such metals behave in the following way when treated anodically with a current density above that limiting value below which no passivation occurs. The metal dissolves as ions at the normal potential of the lowest of the usual valency values exhibited by that metal. This process continues for some time which latter is usually determined by various factors, when suddenly

the potential becomes more positive, the metal stops going into solution as ions of low valency and now either passes into solution as ions with a higher valency or becomes inert and the current is employed in liberating anions with the subsequent formation of oxygen. The anodic behaviour of iron and chromium is perhaps best known in this connection.

(3) The third group is comprised of those metals which are electrochemically inert in most electrolytes. On being anodically polarized such metals do not dissolve to any appreciable extent, but rapidly attain moderately high positive potentials with the subsequent evolution of oxygen. The wide application of platinum in electrochemistry is made possible by its inert behaviour which is typical of all the metals of the platinum group.

Extensive studies have been made in the anodic behaviour of platinum, among other metals, in order to elucidate the mechanism of anodic evolution of oxygen and to ascertain the causes of the irreversibility of the oxygen electrode.

A cell consisting of a reversible hydrogen electrode and a reversible oxygen electrode immersed in the same electrolyte, both gases being at 760 m.m. pressure, should have an E.M.F. = 1.227 volt at 25°C. which is the value of the decomposition voltage of water calculated thermodynamically by Lewis and

Randall [1]. Experimentally this value has never been obtainted. Various workers have found values for the E.M.F. of the oxygen-hydrogen cell ranging from 0.98 volt to 1.08 volt, while the value of 1.14 volt has been obtained after the cell had been allowed to stand for some time. The well-known fact of the thermodynamical reversibility of the hydrogen electrode suggests that the anomalous behaviour of the oxygen-hydrogen cell is to be traced to the oxygen electrode.

Moreover, this behaviour of the oxygen electrode does not depend on the nature of the inert metal to any extent, but is shown with bright iridium and iridised electrodes as well as with platinised and bright platinum electrodes.

Many theories have been advanced to account for the observed data but the most widely held view is that oxides of platinum are formed on the electrode which thus never becomes saturated with oxygen and thus never reaches the reversible oxygen potential. A fair amount of evidence appears to support this view-point. Grube [2] found that the various platinum oxides gave electrode potentials which were not far removed from that of a platinum electrode in a saturated solution. Lorenz and his co-workers also noted a similarity between the electrode potentials of platinum in oxygen saturated sulphuric

acid and sodium hydroxide solutions and those of the hydrated platinum oxides when measured against a hydrogen electrode in the same solutions. The values for the E.M.F.'s of the following four cells approximate to the experimental value found for the oxygen-hydrogen cell.

H_2, Pt	$N.H_2SO_4$	PtO aq.	E.M.F.=1.017	volt
H_2, Pt	$N.H_2SO_4$	PtO aq.	0.894	"
H_2, Pt	N.NaOH	PtO aq.	1.100	"
H_2, Pt	N.NaOH	PtO aq.	0.949	"

Haber and his co-workers [4] using glass and fused alkali as electrolyte measured the E.M.F. of the oxygen-hydrogen cell at temperatures from 300° to 1000° C.

Under these conditions he found that the values obtained were very close to the calculated E.M.F. 's, which lends support to the oxide theory as it is very probable that the oxides are unstable at these high temperatures.

However if a platinum electrode immersed in an oxygen saturated solution very quickly acquires a film of oxide, it would be expected that a more profitable line of investigation would be to study the behaviour of the so-called inert metals when anodically polarized. Several workers have pursued such methods and it is only necessary to mention a few of their findings at this stage. Both Grube[2] and Lorenz[3] have studied the decay of potential of

platinum electrodes after having been anodically polarized. They both came to the same conclusion, namely that the steady fall of potential with time had its origin in the decomposition of oxides which had been formed during the anodic polarization and had formed solid solutions with the platinum or with each other. Foerster(5) working along similar lines, anodically polarized platinised and iridised electrodes, removed them from the solution, placed them in fresh sulphuric acid solution and noted the rate at which their potentials decayed. He found that the potential of the platinum electrode fell after some days to the steady value of +1.08 volt while that of the iridium fell more rapidly to +0.86 volt. He also interpreted this behaviour as due to the formation of labile peroxides which were soluble in the finely divided metals and the slow decomposition of the peroxides into oxygen and more stable lower oxides. In this respect the peroxide of platinum was more stable than that of iridium.

Jirsa(5a), comparing the anodic behaviour of a palladium electrode which had been previously cathodically polarized in normal sodium hydroxide with that of an electrode whose surface had been coated with oxide by heat treatment, came to the conclusion that during the establishment of the oxygen overvoltage a series of oxides of palladium

were formed. However, his method of presenting his results as current density— voltage relationships is not a very good one because the time factor, which is very important near a transition stage from a depolarization process to a polarization process, is not sufficiently emphasized by this method. A pure palladium electrode treated in the above manner shows two depolarization processes before the oxygen overvoltage is attained. The first is due to the formation of palladium sub-oxide Pd_2O, and the second to that of PdO ; these oxides are considered to give rise to intermediate oxides as shown by the following scheme :

$$Pd \longrightarrow Pd_2O \longrightarrow PdO \longrightarrow PdO_2 \longrightarrow PdO_3$$
$$+0.15 \quad (0.40\text{-}0.50) \quad +0.95 \quad (1.22) \text{ volts}$$

The PdO_3 is unstable and decomposes into PdO_2 and oxygen.

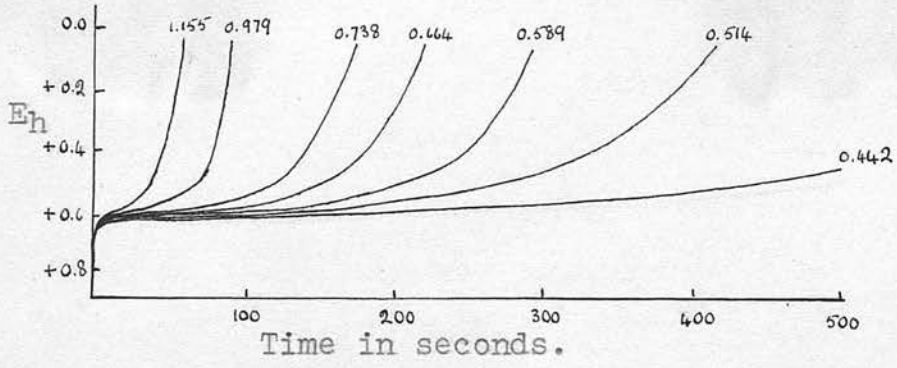
More recently, Hoar[6] has attributed the low potential of the oxygen electrode to the fact that a platinum electrode is covered by an oxide film some molecules thick which may be expected to contain cracks and pores pervious to the electrolyte. A cell will therefore be set up consisting of exposed metal, electrolyte and film which latter will be cathodic towards the metal owing to the presence of adsorbed oxygen. Current will therefore flow between the film and metal with cathodic dissolution of oxygen at the

film surface and a consequent fall of its potential. The net result at the metal surface will be oxide formation at a rate equivalent to the current flowing. This irreversible oxide formation then leads to the low oxygen potential at such a film surface. The anodic current which must be supplied to such a system to maintain it at the reversible oxygen potential will depend on the rate at which the pores can be closed up by oxide formation and a relationship between this current and the time has been deduced. The experimental results show a fair amount of agreement with the theory outlined above.

Bowden[7] has examined the anodic and cathodic behaviour of platinum electrodes in sulphuric acid. If a platinum electrode is polarized anodically in sulphuric acid to the stage at which oxygen is liberated and the current is then reversed a definite depolarization stage occurs at about E_h = +0.60 volt. The length of this depolarization process depends on the previous anodic treatment, and Bowden suggests that it is due to the reduction of an oxide which has been formed during the anodic polarization.

Butler, Armstrong and Himsworth[8][9] have

studied the behaviour of platinum electrodes in sulphuric acid and alkaline solutions containing oxygen. They find that in sulphuric acid when a new platinum electrode is polarized anodically the potential rapidly reaches the steady value at which oxygen is liberated. On reversing the current the potential rapidly changes to E_h = +0.60 volt when a depolarization process sets in and continues for some time before the potential rises to the point at which hydrogen is deposited. When the electrode is made cathodic once more, the potential falls rapidly to E_h = +0.85 volt and then linearly at a much slower rate to E_h = +1.50 volt where it remains constant and oxygen is evolved.



The figures at end of the curves give the currents employed in milliamps.

fig. 1.

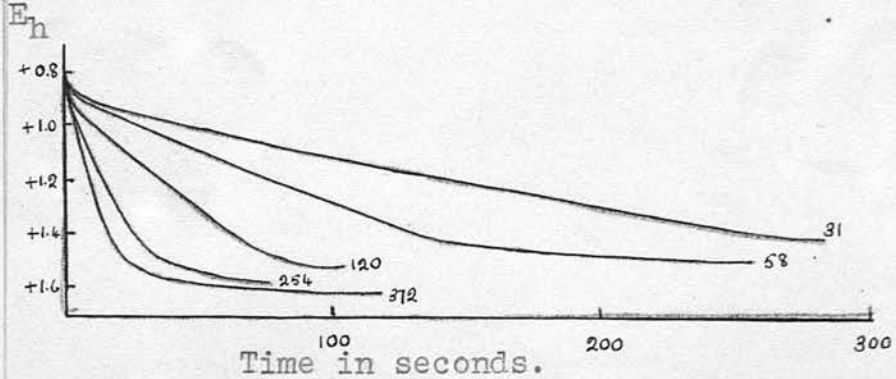
The cathodic behaviour of platinum in oxygen

saturated sulphuric acid solution after a short anodic polarization is shown in fig.1. Bowden(7) suggested that the depolarization process beginning at +0.60 volt is due to the reduction of a platinum oxide PtO_2 which is formed during the anodic process, but Butler and Armstrong (8) have shown that this is very improbable as the length of this process is reduced to a considerable extent even by gently stirring the solution. Moreover in some of Bowden's experiments the quantity of electricity passed during this reduction stage was of an order that would be required for the reduction of a layer of oxide thirty molecules thick. It is possible that such a thick oxide film would be visible, but no difference in the condition of the electrode surface could be discerned. The dependence of the length of this arrest on the cathodic current density together with the general course of the curve have led Butler, Armstrong and Himsworth (9) to the conclusion that the depolarization is due to oxygen dissolved in the solution. The electromotive activity of dissolved oxygen would appear to be greater at a platinum electrode, which has been polarized anodically for a short time, than at a new unpolarized electrode. This depolarization process is similar to the cathodic depolarization at platinum electrodes produced by solutions of methylene blue and quinhydrone and the length of the process to the final rapid rise of potential is given by the equation:

$$it = A + Bt$$

where i is the current, t is the transition time which is the time taken to reach an arbitrarily chosen potential on the rapidly rising part of the curve and A and B are constants. The slope B is approximately equal to the concentration of the depolarizer and A is the amount of electrolysis which is required to establish the diffusion layer at the electrode surface.

After the cathodic depolarization process described above a considerable amount of anodic polarization is required to bring the potential to a steady value. The anodic curves are linear from +0.85 and their slopes depend on the current density as shown in fig.2.



The figures at end of the curves give the currents employed in amps. x 10^{-7}.

Fig.2.

However, the quantity of electricity passed during this linear portion of the curves is approximately constant and independent of the current density. The quantity of electricity required to change the potential by a given amount in this region is approximately fifteen times that required to charge the double layer and is equal to the amount which would be required to form a complete layer of adsorbed oxygen. This adsorbed layer is removed during the cathodic treatment simultaneously with the depolarization due to oxygen. The behaviour of platinum is similar in alkaline solutions and in solutions of intermediate P_h value.

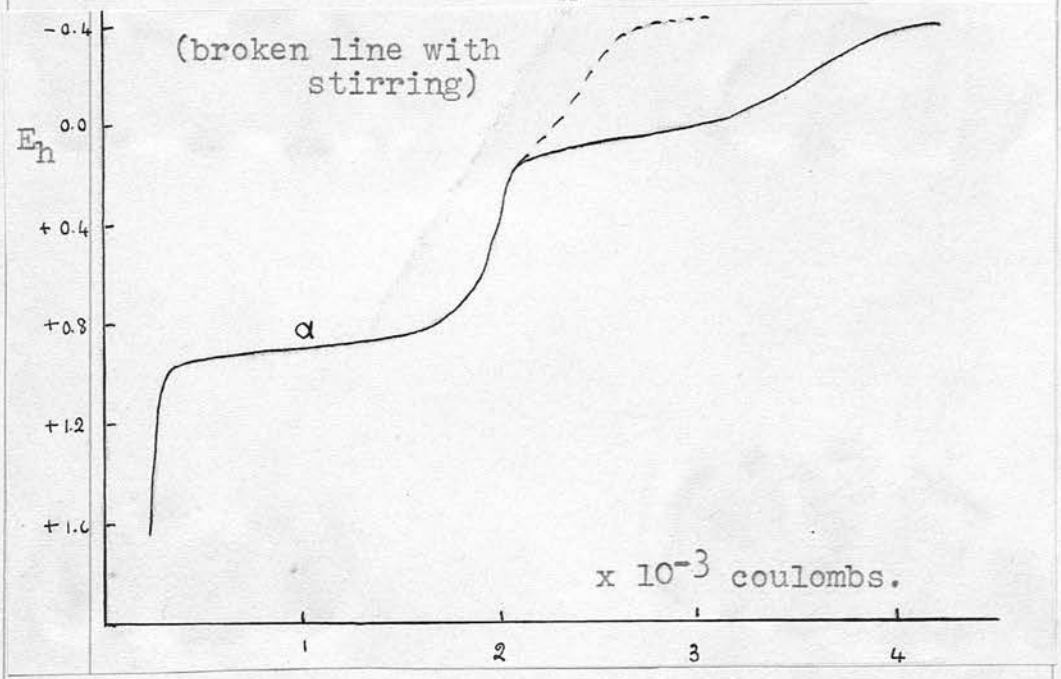


Fig.3.

When platinum was anodically polarized no signs of definite oxide formation were observed.

However gold electrodes when treated anodically in sulphuric acid showed two depolarization processes on cathodic treatment. The upper one commencing at E_h = +0.2 volt (see fig. 3.) is due to oxygen depolarization and is much reduced by stirring. The stage α occurring at E_h = +0.9 is unaffected by stirring and is due to reduction of oxide which has been formed during the anodic treatment. The efficiency of oxide formation measured by the ratio of the amount of electricity required during the cathodic depolarization stage to the total amount of anodic polarization is initially high, approaching 100% but rapidly falls off and ultimately reaches a constant value of 0.9%. With continued electrolysis the oxide becomes visible as a black film on the electrode surface.

This work is a continuation of the investigation of electrode processes along similar lines to those of Butler and Armstrong outlined above. It was thought that it would be profitable to examine the electrochemical behaviour of some of the other so-called inert metals of the platinum group, paying particular attention to the possibilities of oxide formation.

The behaviour of palladium, rhodium and iridium in sulphuric acid and sodium hydroxide solutions was first studied.

Any further introductory matter will appear in the appropriate section.

Experimental.

(1) Measurement of potential changes.

The current densities employed in this work were such that the potential changes were moderately slow. Under these conditions it was found that a Lindemann electrometer in conjunction with a Cambridge Instrument Co. potentiometer was suitable for recording any changes in potential. The arrangement employed is shown in fig. 4.

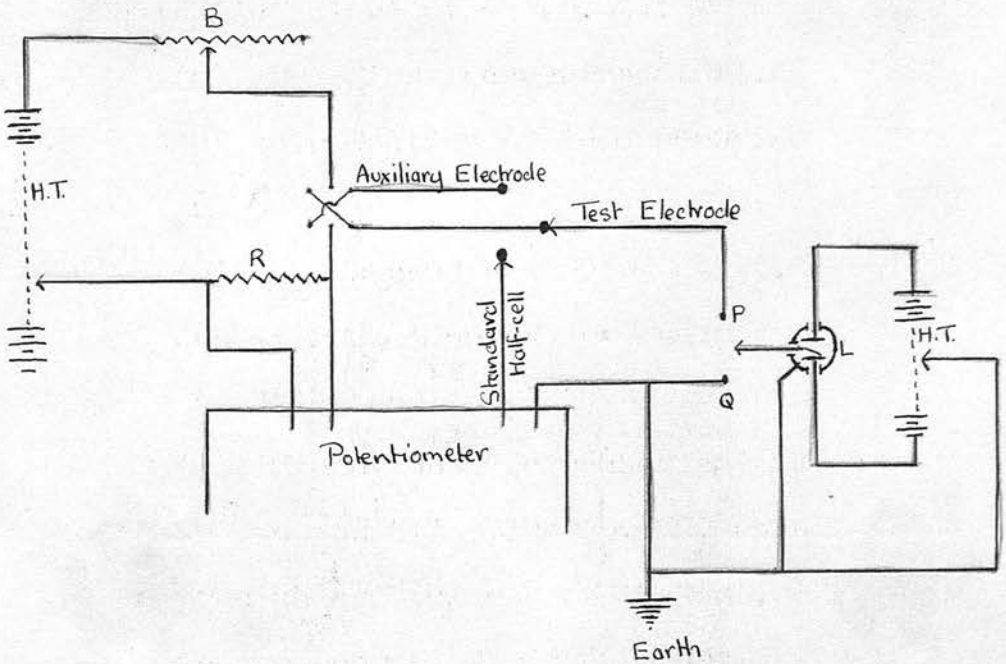


fig. 4.

The needle of the Lindemann electrometer L can be connected through the mercury cups P and Q either

to the test electrode or to earth. A microscope is provided for observing the end of the needle, and when the latter is earthed a zero point can be fixed on the eye-piece scale. This reading can be reproduced, when the needle is connected to the test electrode, by adjusting the voltage reading of the potentiometer which is connected in series between the standard half-cell and earth. The potentiometer then gives the difference of potential between the test electrode and the standard half-cell. The most suitable arrangement resulted when the plates of the Lindemann electrometer were connected to the 90 and 30 volt terminals of an " Ever Ready" dry battery, while the 60 volt terminal was earthed. The sensitivity is about 0.001 volt.

(2) Measurement of polarizing current.

The polarizing current was supplied by an "Ever Ready" H.T. battery (see fig.4) and a wide range of current density was obtained by the introduction of B, a bank of grid leaks, in the polarizing circuit. The polarizing current was measured, after each experiment, on the potentiometer by finding the fall in potential along a suitable known resistance R.

(3) Reference Electrodes.

When the electrolyte was sulphuric acid a mercurous sulphate half-cell in sulphuric acid of the

same concentration was employed as reference electrode. When working with sodium hydroxide as electrolyte a normal calomel half-cell was used as reference electrode. The potential of the mercurous sulphate half-cell $Hg \mid Hg_2SO_4$, M/10 H_2SO_4, against the normal calomel electrode is +0.388 volt. Taking the potential of the normal calomel electrode to be + 0.282 volt on the standard hydrogen scale, the corresponding value of the mercurous sulphate electrode is E_h = + 0.670 volt.

Throughout this work all potential measurements refer to the standard hydrogen scale.

(4) Electrolysis Vessels.

The electrolysis vessels used in this work were of the simplest type, as shown in fig.5.

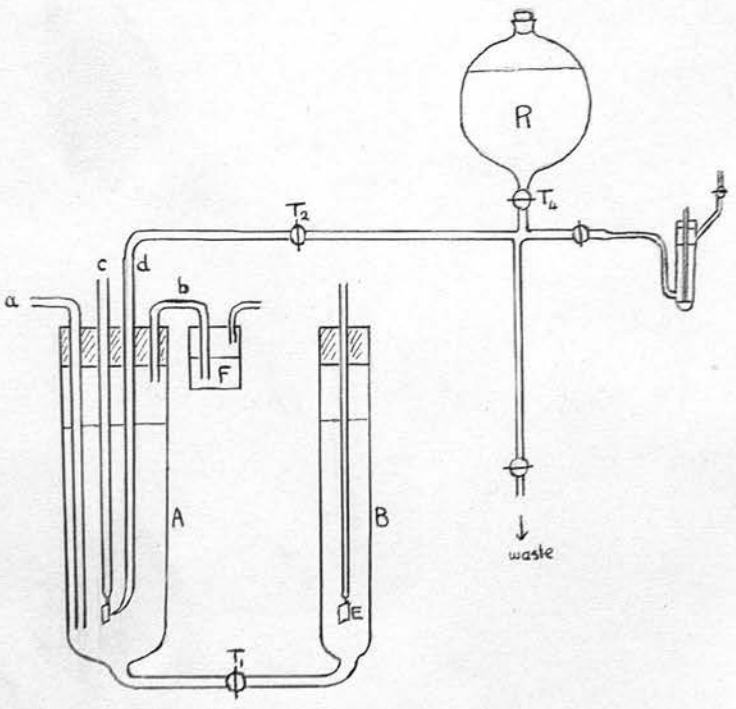


Fig.5.

The vessel consisted of two compartments A and B. The former measuring 6" x 2" diameter contained the test electrode and the latter measuring 6" x 1" diameter contained the auxiliary electrode E which was always of platinum foil. The two compartments were separated by a tap T_1, which was normally kept closed, sufficient conduction being obtained around the barrel. The rubber stopper in A carried four tubes. a and b were used as inlet and outlet tubes for oxygen or nitrogen; b was fitted with a gas trap F. The electrode was sealed into the tube c, while contact between theelectrolyte and standard half-cell was made through the tube d, the end of which was brought into close contact with the surface of the electrode in order to minimise resistence effects due to ohmic drops in potential.

After charging the vessel with electrolyte and fitting the rubber stopper, the solution was sucked up through d past the tap T_2 to the right-angled bend. The tap T_2 was then closed and T_4 opened until contact between the solution in the reservoir R and the electrolyte in A was made at the junction.

During an experiment all taps were kept closed to prevent any diffusion process taking place.

The whole apparatus was insulated by placing it on sheets of plate glass supported on paraffin blocks.

(5) Electrodes

With the exception of palladium, electrodes of all the metals were made by cutting an L-shaped piece from the foil (see fig.6). The upper limb was soldered onto copper wire and sealed into a glass tube with wax, so that only the lower limb was exposed to the solution. The dimensions of this exposed rectangle were 1cm. x $\frac{1}{2}$cm. giving a total electrode area (apparent) of 1cm^2. The palladium electrodes were made by spot-welding a piece of palladium foil measuring 1cm. x $\frac{1}{2}$cm. on to palladium wire which was then melted into a glass tube.

Fig.6.

(6) Electrolytes.

The electrolyte was either oxygen saturated M/10 sulphuric acid or N/5 sodium hydroxide. The oxygen used in the experiments was obtained from a cylinder of the gas. Sometimes the solution was stirred with nitrogen to displace most of the oxygen. As it was not necessary to purify the nitrogen from traces of oxygen the gas was bubbled into the electrolysis vessel directly from the cylinder.

Palladium in oxygen saturated M/10 sulphuric acid solution

The general behaviour of palladium electrodes on anodic polarization in this solution is shown in fig.7 where the potentials of the electrodes on the standard hydrogen scale are plotted against the time in seconds. The figures after the numbers of the curves refer to the polarizing current in microamps., and where such figures appear later they will always refer to the polarizing current.

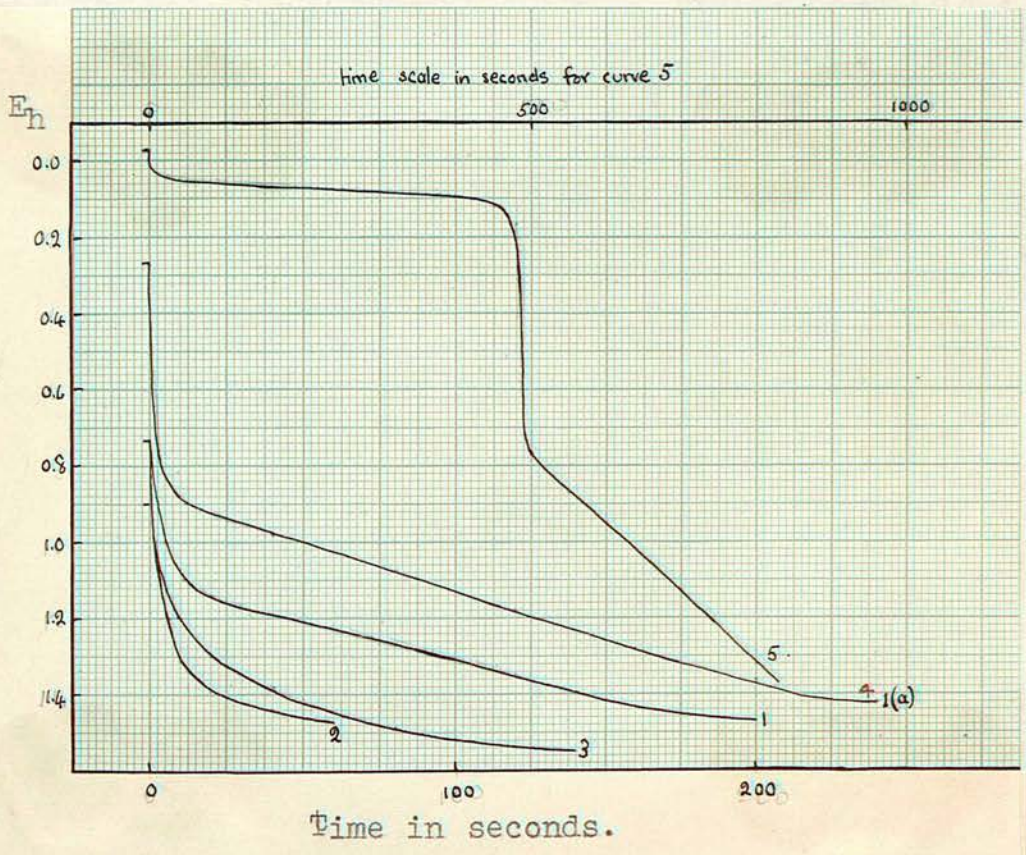


Fig.7.

The steady potential attained by a palladium electrode in this solution was E_h=+0.74 volt. On making the electrode anodic with a current density of 15 microamps./cm^2. a considerable amount of

depolarization takes place before the potential approaches a constant value (curve 1) at E_h= +1.51 volt, which represents a considerable oxygen overvoltage. On allowing the overvoltage to decay to +0.77 volt and then applying an anodic current of 9.5 microamps/cm^2. (curve 2), the potential falls much more rapidly than in the first experiment. Only 24 seconds were required for the potential to reach+ +1.40 volt in the second experiment whereas in the first experiment with a larger current, 142 seconds elapsed before this value was reached.

Although the behaviour of an electrode was not very reproducible when first in use, it was found that after a few experiments the reproducibility was very good indeed.

Curve 1(a) shows the potential changes taking place on anodic polarization after the electrode had been previously cathodically polarized to +0.27 volt. The cathodic polarization made the subsequent anodic curves, obtained with a large range of current densities, very reproducible. Curve 5 was obtained after the electrode had been made cathodic to the stage at which hydrogen could be liberated. The hydrogen is absorbed by the palladium and is removed during the subsequent anodic polarization while the potential remains constant at +0.10 volt.

Effect of current density on anodic behaviour of palladium.

In this series of experiments the following procedure was adopted. Before each experiment the electrode was made cathodic to +0.37 volt with a current density, i = 200 microamps./cm.^{2}, it was then polarized anodically to +1.45 volt and finally the solution was stirred by bubbling a stream of oxygen through it. The results are shown in fig. 8.

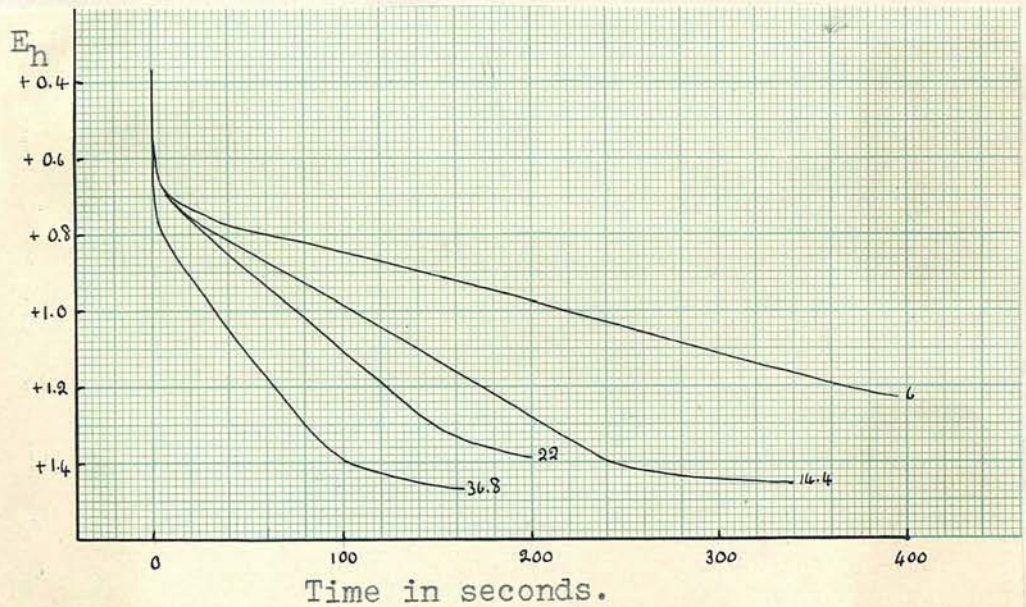


Fig. 8.

Under the above conditions the behaviour of the electrode is very reproducible and all the curves show the following characteristics. The potential changes rapidly to +0.75 volt and then more slowly and linearly to a value at which oxygen evolution commences where the potential then remains constant. The slopes of the curves decrease with decreasing

current densities and the quantity of electricity required to change the potential by 0.10 volt on this linear part is approximately constant as the results in table 1 show.

Table 1.

current	6.0	14.4	2.20	36.8 microamps.
coulombs for 0.10 volt	4.32	4.92	5.28	5.52×10^{-4}

The quantity of electricity passed during the linear portions of the curves is about 30.0×10^{-4} coulombs.

Effect of previous cathodic treatment on subsequent anodic polarization.

The electrode was made cathodic to increasingly negative potentials with a current of 200 microamps. and then anodically polarized with a current density of 9.5 microamps. per cm^2 .
The variation of potential with time is shown in fig. 9.

Only when the electrode has been taken cathodically to points on the depolarization curve do we find any increase in the quantity of electricity required to change the potential by 0.10 volt over that required for charging the double layer. The capacity of the double layer is found by allowing the oxygen overvoltage to decay and then making the electrode anodic once more with a small current. This quantity is 1.8×10^{-5} coulombs / 0.10 volt.

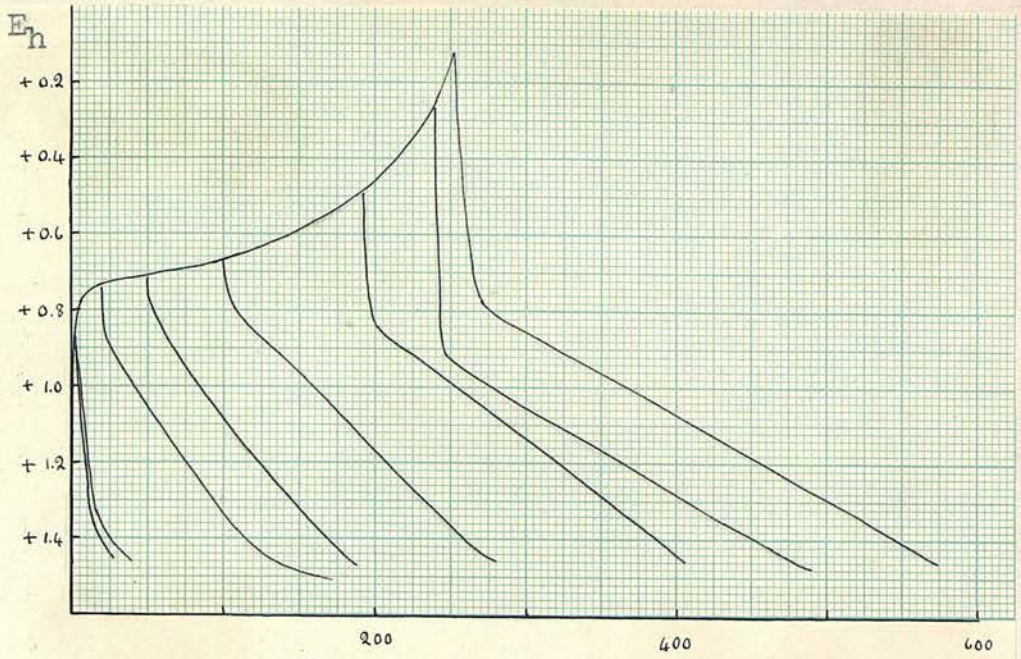


Fig. 9.

On now going towards more negative values we find a steady increase in the amount of electricity required to effect the potential change during the subsequent anodic polarization. This is most clearly seen in table 2.

Table 2.

initial voltage	+0.07	+0.27	+0.47	+0.64 volt
slope	4.18	4.18	3.28	2.33×10^{-4} coulombs per 0.10 volt
initial voltage	+0.68	+0.69	+0.77	+0.82 volt
slope	1.90	1.57	0.34	0.34×10^{-4} coulombs per 0.10 volt

Cathodic behaviour of palladium in oxygen saturated M/10 sulphuric acid.

The variation of potential with time during cathodic polarization after the electrode has been made anodic to +1.45 volt is shown in fig.10.

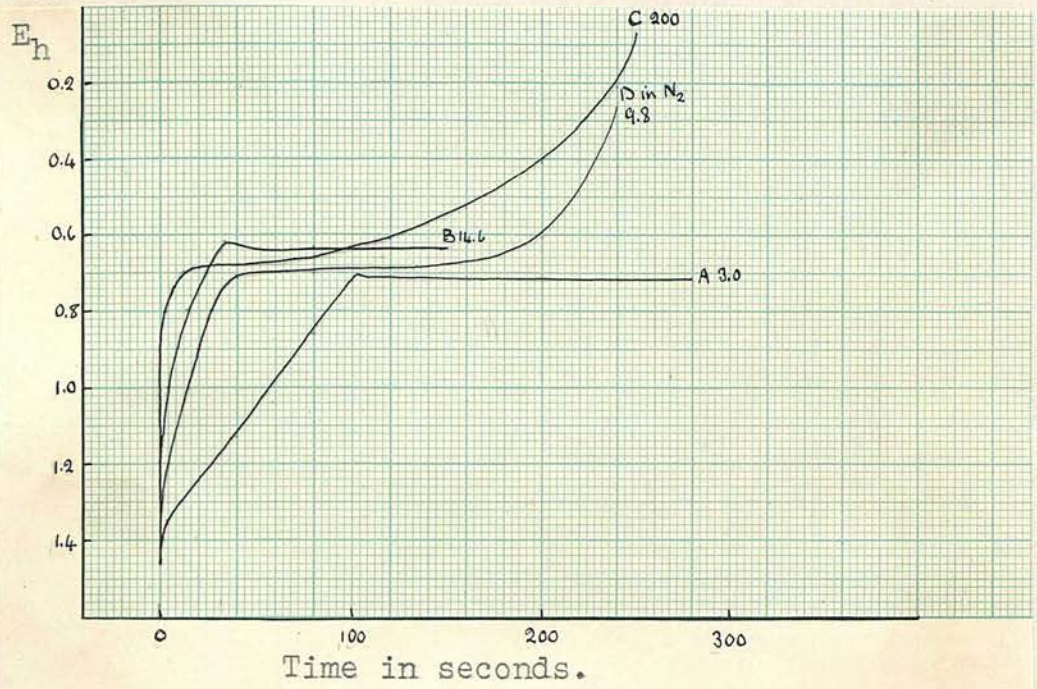


Fig.10.

The potential changes rapidly and linearly to +0.70 volt or thereabouts after which a depolarization process sets in. The duration of this depends on the current density and represents the cathodic depolarization due to oxygen dissolved in the electrolyte. Curves A, B and C were obtained in oxygen saturated solution, and curve D in nitrogen saturated solution.

This depolarization process is similar to that which takes place at platinum electrodes[9] and was not studied in detail.

However, when a palladium electrode has been polarized anodically for some time with somewhat larger current densities (ca. 700 x 10^{-6} amps./cm.^{2}) another depolarization process, occurring at potentials less negative than that required for depolarization due to oxygen in the electrolyte is observed. This new depolarization process occurs between +1.60 volt and + 0.65 volt and is not nearly so marked as the oxygen depolarization which commences where the former process ends. The quantity of electricity required to raise the potential of the electrode to +0.72 volt (see fig.11.) increases with amount of anodic polarization and is greater than that required for the same purpose after an anodic polarization with a smaller current. The curves in fig.11 correspond to

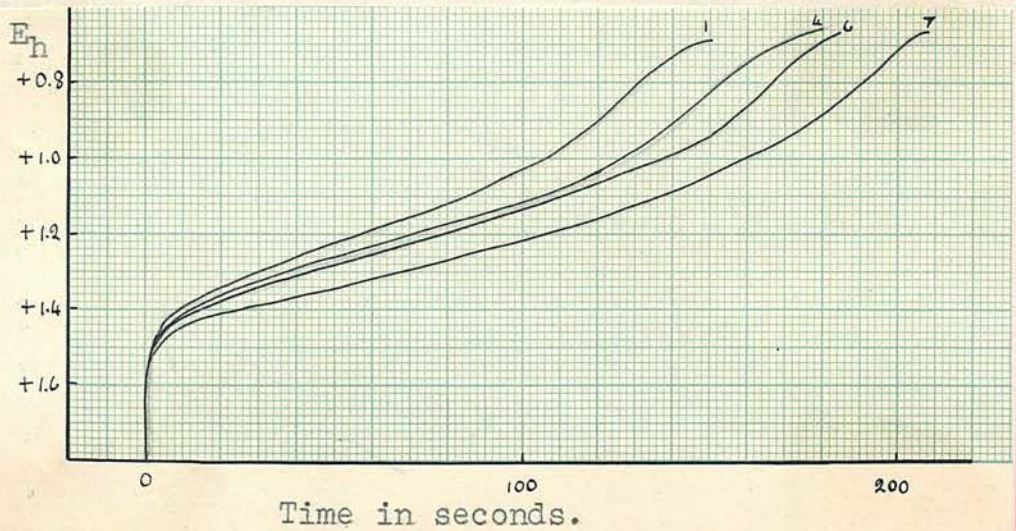


Fig.11.

the experiments marked with an asterisk in table 3.

Table 3 shows the results of a series of experiments in which the electrode was made anodic with a c.d. of 697×10^{-6} amps./cm.^{2} for various periods of time and then cathodically polarized with a small current, 5×10^{-6} amperes. The second column gives the quantity of electricity passed during the anodic treatment and the last column gives the quantity required to bring the potential to E_h = +0.72 volt, i.e. to complete the first depolarization process.

Table 3 (Series A)

Experiment	Anodic coulombs	Cathodic coulombs to +0.72 volt
1*	41.8×10^{-3}	7.0×10^{-4}
2	83.1	7.5
3	125.5	8.0
4*	167.3	8.2
5	209.1	8.3
6*	418.2	8.8
7*	1254.6	10.0

The quantities found in the last column are greater than the quantity required to bring the electrode potential to the same value after having been made anodic with a current of 10×10^{-6} amperes; this quantity was about 2×10^{-4} coulombs. These experiments suggest that a small amount of oxidation occurs during the anodic process and that the oxide

is reduced during the cathodic polarization. The last column in table 3 then gives a measure of the extent of oxide formation and it is obvious that comparatively large increments in the amount of anodic treatment only effect very small increases in oxide formation.

A few experiments were made to determine whether the oxide was soluble in the acid solution used. In each experiment the electrode was made anodic with i = 700 microamps. for three minutes, the polarizing circuit was then opened and varying intervals of time were allowed to elapse before the electrode was made cathodic with i = 5 microamps. The effect of stirring by bubbling nitrogen through the electrolyte was also noted. The results are shown in table 4.

Table 4.

Experiment	Interval before cathodic		Time to reach +0.72 volt
1	0 mins.		148 secs.
2	9 "		78 "
3	90 "		13 "
4 *	10 secs.	stir during interval	119 "
5	5 mins.	"	71 "
6	13 "	"	31 "
7 *	0 "	stir during cathodic	122 "

The last column gives the times required to reach +0.72 volts during cathodic polarization, i.e. it gives the amounts of oxide remaining on the electrode after each interval. It is obvious from the above figures that the oxide is fairly soluble in acid as shown by the reduced cathodic times after stirring and allowing an interval to elapse. In fig. 12 the cathodic times are plotted against the period allowed to elapse between the breaking of the anodic current and the making of the cathodic.

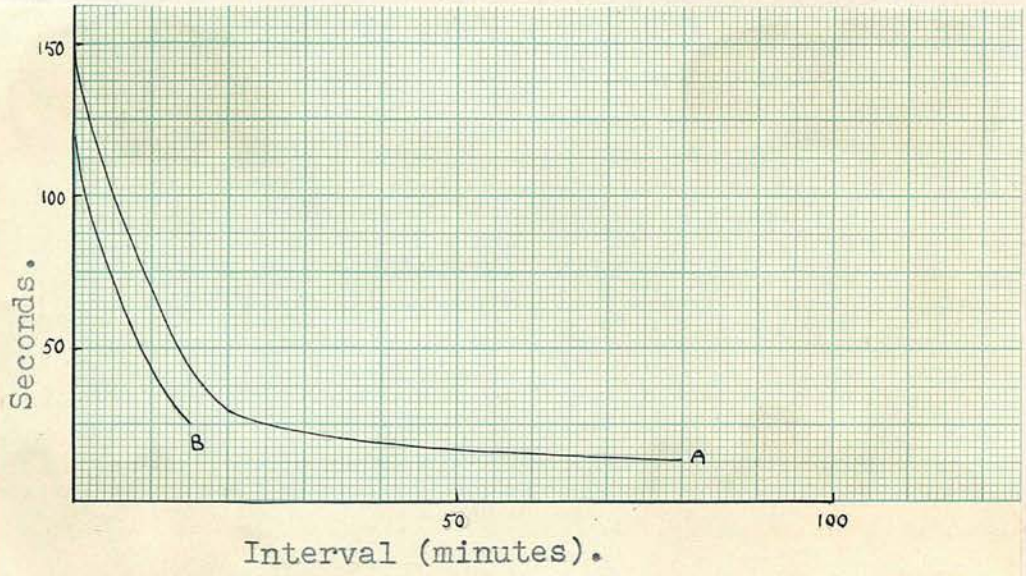


Fig.12.

A - interval alone.

B - with stirring during interval.

Fig.12 together with the experiments denoted by an asterisk in table 4 show that the first 10 seconds, or so, of the stirring is the deciding factor in determining the difference between the effect of

stirring during the interval and an interval alone. The stirring curve is parallel to the interval curve but 28 seconds below it, and it appears that the oxide, in addition to being soluble in acid, is in such a mechanical condition on the electrode surface that one fifth of it can be easily removed by vigourously stirring the solution around the electrode.

It might be thought that the oxide would be less soluble in alkali and could be therefore more readily studied in such a solution. With this object in view similar experiments were carried out in N/5 sodium hydroxide.

Palladium in N/5 sodium hydroxide.

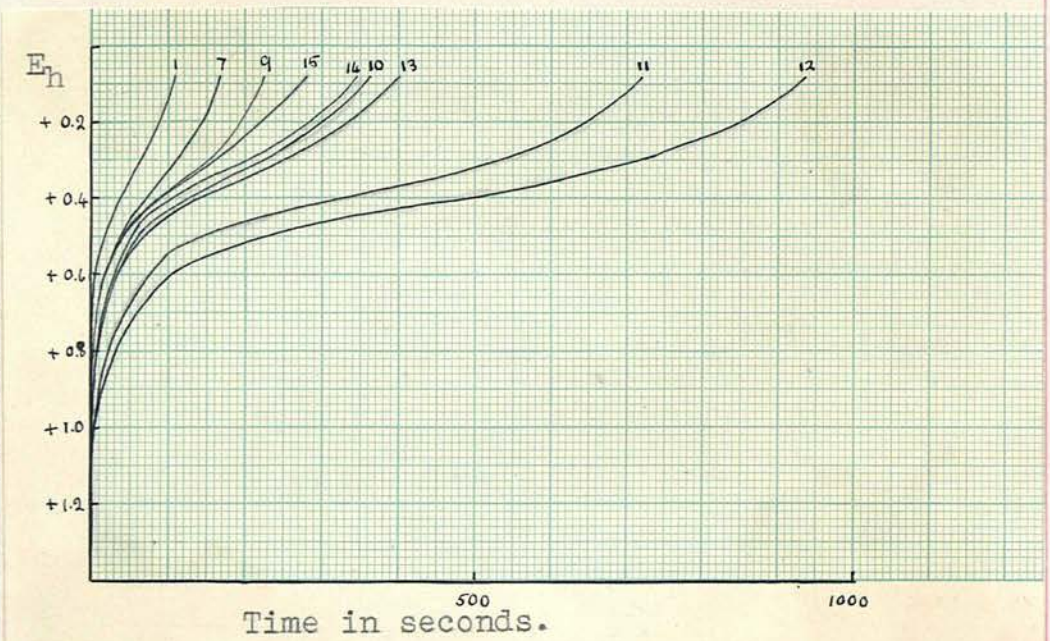
It was soon observed that oxide was formed in alkali as well as in acid, and consequently experiments were made to determine to what extent the oxide was soluble in this solution. The results of table 5 show that the oxide is in fact much less soluble in alkali than in acid solution.

Table 5.

Interval before cathodic	time to reach +0.05 volt
0 seconds	203 seconds
5 minutes	187 "
10 seconds(stirring)	203 "
5 minutes "	187 "

In each experiment the electrode was made anodic with a current of 542 microamps. for 10 minutes and then cathodically polarized with a current of 4 microamps.

A series of experiments was made to determine the extent of oxide formation with increasing amounts of anodic treatment. The electrode was anodically polarized with i = 540 microamps. for varying times and then made cathodic with a small current, 4.8 microamps. Some of the return cathodic curves obtained are shown in fig.13.



Fig,13.

The numbers on the curves refer to the experiments in table 6 where the total amounts of electricity passed during the anodic treatment and the quantities required to reduce the oxide are tabulated.

Table 6. (Series B)

Expt.	Coulombs passed during anodic treatment	Coulombs required to reach +0.08 volt
1	10.8×10^{-3}	5.30×10^{-4}
2	21.6	5.56
3	32.4	5.86
4	64.8	6.23
5	129.6	6.72
6	194.4	7.00
7	550.0	7.58
8	1296.o	8.73
9	2592.0	10.54
10	4880.0	16.70
11	11600.0	33.70
12	20500.0	43.50
13	324.0	18.60
14	162.0	17.20
15	32.4	13.10

the experiments were made in the above order and it is obvious from the last three experiments that a greater amount of oxidation has taken place than in corresponding experiments made earlier in the series. This effect is more clearly seen in table 7 which embodies the results of a series of consecutive experiments in which the electrode was made anodic with a current of 530 microamps. for 1, 7,15,30,60,96,60,30,15,7 and 1 minute, after which

a cathodic current of 4.8 microamps. was passed.

Table 7 (Series C)

Expt.	Coulombs passed during anodic treatment	Coulombs required to reach +0.08 volt
1	31.8×10^{-3}	6.24×10^{-4}
2	222.0	7.90
3	476.0	8.45
4	952.0	9.85
5	1904.0	12.95
6	3050.0	23.30
7	1904.0	28.30
8	952.0	28.30
9	476.0	27.20
10	222.0	24.50
11	31.8	20.70

Rhodium in oxygen saturated M/10 sulphuric acid.

The equilibrium potential of a rhodium electrode in this solution is +0.80 volt. The behaviour of rhodium on anodic and cathodic polarization is similar to that of palladium as is shown by the curves in fig.14.

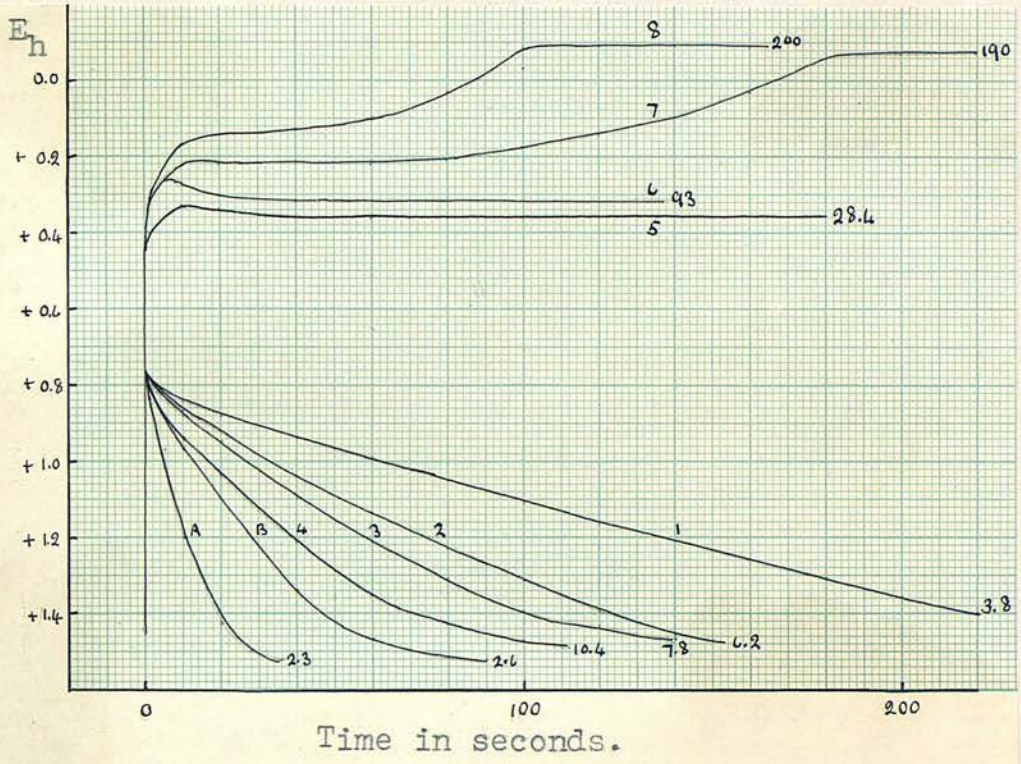


Fig.14.

Curves 1 - 4: anodic polarization from -0.03 volt.
" B " " " +0.37 "
" A " " " +0.57 "
" 5 - 8: cathodic " " + 1.50 "

(figures at end of curves refer to current densities in microamperes per cm^2.)

When the electrode is first made anodic a considerable amount of depolarization takes place before the potential reaches a steady value. When the overvoltage is allowed to decay and the electrode

again made anodic, the potential rapidly falls to the oxygen overvoltage for that current density. The anodic curves were not reproducible unless the electrode had been made cathodic to -0.03 volts (hydrogen liberation at this electrode with a current density of 200 microamps. took place at E_h = -0.10).

The effect of current density on the slope of the anodic curves is shown in table 8.

Table 8.

current density	3.5	6.2	7.88	10.4 microamps. per cm^2
slope of curve	1.33	1.30	1.29	1.25×10^{-4} couls./0.1 volt

The quantity of electricity required to take the potential along the linear parts of the curves is 9×10^{-4} coulombs. The capacity of the double layer as measured by the quantity of electricity required to establish the oxygen overvoltage after it has been allowed to decay is 1.2×10^{-5} coulombs/ 0.1 volt.

When the electrode is made cathodic after an anodic polarization with a small current, the depolarization due to oxygen in the solution commences in the neighbourhood of +0.30 volt (fig.14); this is a rather more negative value than was found for palladium in this solution (+0.70 volt).

Rhodium in N/5 sodium hydroxide.

The general behaviour of rhodium when polarized with small currents in this solution is similar to that in sulphuric acid. However after anodic polarization with larger current densities (ca.1000 microamps./cm^2) the subsequent cathodic curves show another depolarization process occurring at more positive potentials than that due to oxygen in the solution. This appears to be due to the reduction of an oxide formed during the anodic treatment.

The effect of an interval between the breaking of the anodic and the making of the cathodic current is shown in table 9. The anodic current was 1320 microamps. for one minute and the cathodic was 15 microamperes.

Table 9.

Interval before cathodic	Time to reach +0.08 volt
0 minutes	94 seconds
1 "	84 "
6 "	70 "
1 " (with stirring)	76 "

These results show that the oxide is somewhat soluble in alkali.

The curves in fig.15 show the effect of varying amounts of anodic treatment on the length of the cathodic breaks. The anodic and cathodic currents were of the same magnitude as the above.

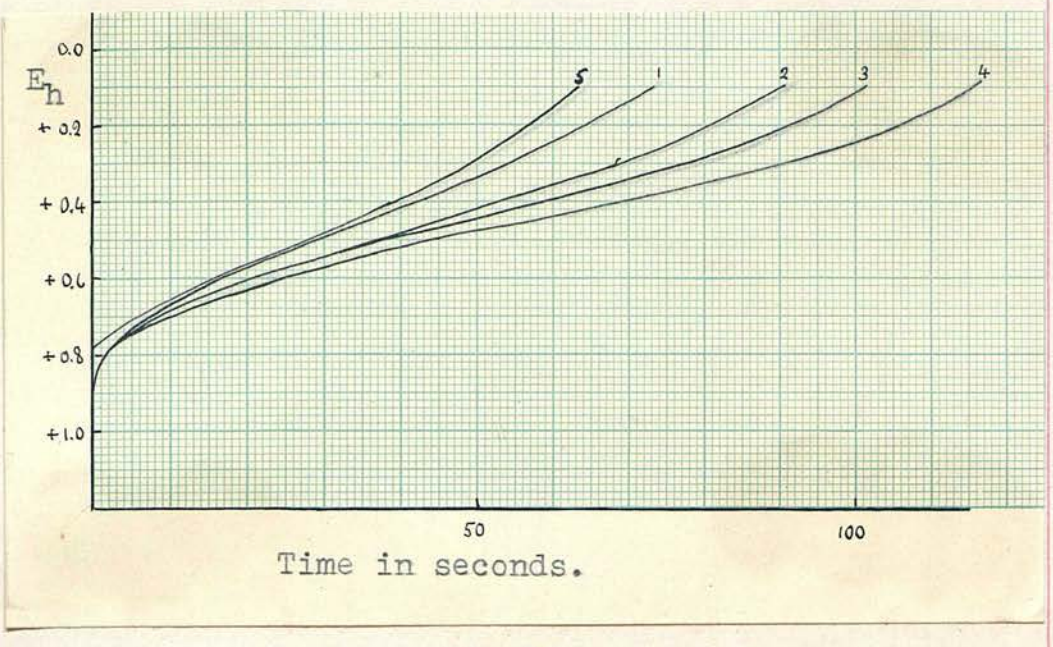


Fig.15.

The figures after each curve refer to the experiments in table 10, in which the last column gives the number of coulombs required to reach +0.08 volt.

Table 10 (Series D)

Experiment	Anodic coulombs	Cathodic coulombs to reach +0.08 volt
1	79.2×10^{-3}	11.7×10^{-4}
2	396.0	14.1
3	1188.0	15.4
4	2772.0	17.7
5	1.3	7.1

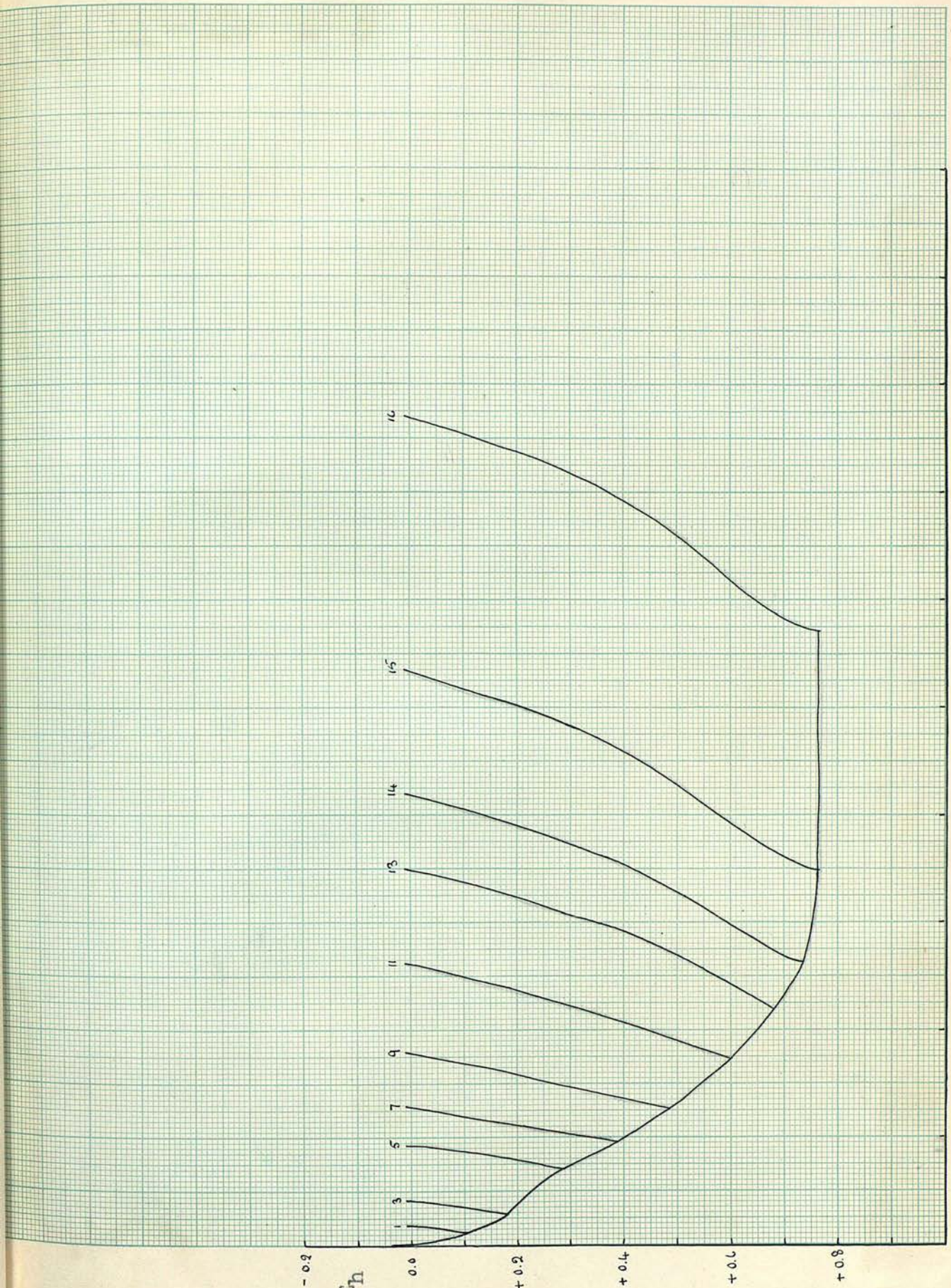
The potential at which oxygen begins to act as depolarizer in this solution is in the region of -0.10 volt. Experiment 5 was made with an anodic current of 10.7 microamps. for two minutes and then cathodic with the same current. The quantity 7.1 x 10^{-4} coulombs is much greater than was formerly required to reach this potential in earlier experiments with smaller currents and it is obvious that the anodic treatment with larger currents has activated the electrode in such a manner that a certain amount of oxidation with smaller anodic currents is readily produced.

Table 11 shows the effect of anodic current density on the amount of oxide formed.

Table 11 (Series E)

Expt.	Current (microamps.)	time of anodic	coulombs anodic	coulombs cathodic
1	10.7	1 min.	0.6×10^{-3}	5.6×10^{-4}
2	10.7	2 "	1.3	7.1
3	24.2	2 "	2.9	7.6
4	74.4	2 "	8.9	8.6
5	163.0	2 "	19.6	9.0
6	256.0	2 "	30.7	9.5
7	556.0	2 "	66.7	9.8
8	1250.0	2 "	150.0	10.6
9	1250.0	6 "	450.0	11.7
10	1250.0	2 "	150.0	11.1

The marked effect of alternate oxidation and reduction on the subsequent oxidisability of the metal is well shown in fig.16. The electrode was made anodic with a current of 10.4 microamps. to increasingly positive potentials at which the current was reversed and the time required to reach -0.02 volt noted. The figures after the curves refer to the experiments in table 12. The third column gives the total amounts of electricity passed during the anodic polarization. This quantity includes that which is used in forming the adsorbed oxygen layer and since the two quantities are of the same order, the latter which is given in the fourth column must be subtracted from the former if any comparison is to be made between the anodic treatment producing oxidation and the reduction of the oxide by the cathodic treatment which is given in the last column. It should be pointed here that the layer of adsorbed oxygen is not removed until the potential, at which oxygen acts as a depolarizer, is reached. The electrode was made cathodic to -0.52 volt in order to remove both adsorbed oxygen layer and oxide before each experiment.



(Fig. 16)

Table 12 (Series F)

Expt.	potential at which current is reversed	Q_1 anodic coulombs	Q_2 coulombs for adsorbed layer	Q_1-Q_2 coulombs	cathodic coulombs to -0.02 volt
1	+0.18 volt	3.12×10^{-4}	1.50×10^{-4}	1.62×10^{-4}	1.46×10^{-4}
2	+0.23	6.34	2.25	4.09	2.08
3	+0.28	7.70	3.00	4.70	2.40
4	+0.33	8.95	3.75	5.20	3.12
5	+0.38	9.90	4.50	5.40	3.75
6	+0.43	11.42	5.25	6.17	4.79
7	+0.48	13.00	6.00	7.00	6.04
8	+0.53	14.43	6.75	7.68	7.40
9	+0.58	18.20	7.50	10.70	9.17
10	+0.63	20.20	8.25	11.95	11.43
11	+0.68	22.90	9.00	13.90	13.82
12	+0.73	27.50	9.00	18.50	16.56
13	+0.76	36.50	9.00	27.50	19.28
14	+0.77	59.60	9.00	50.60	21.10

In another series of experiments immediately following, in which the procedure was reversed i.e. experiment 14 was the first one and experiment 1 the last, practically the same values were obtained for the quantities in the last column.

Iridium in M/10 sulphuric acid

The behaviour of iridium, when polarized with the smaller currents in this solution, is very similar to that of palladium and rhodium.(see fig.16).

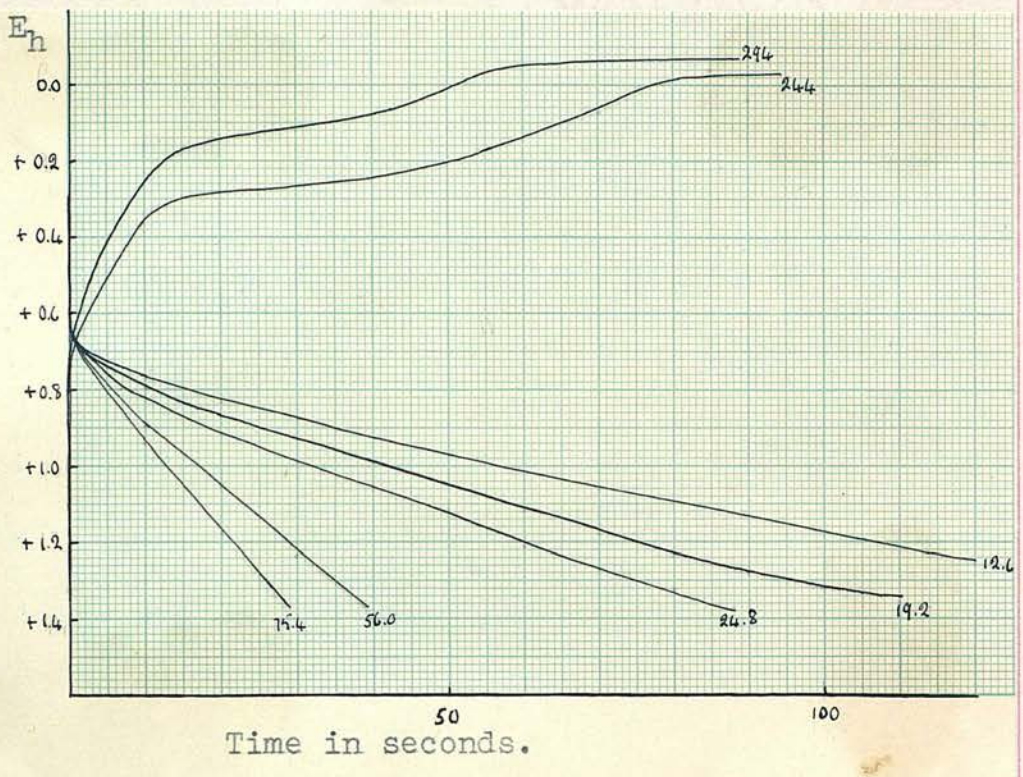


Fig.16.

It was noted, however, that the anodic curves were not very reproducible unless the electrode had been made cathodic to near the reversible hydrogen potential. When this had been done the curves were very reproducible and linear from +0.70 volt to +1.40 volt during which the quantity of electricity passed,

22×10^{-4} coulombs, was independent of the current density.

The slopes of the anodic curves are given in table 13.

Table 13.

current density	75.4	56.0	24.8	19.2	12.6×10^{-6} amps./cm^2
couls./ 0.1volt	3.02	3.08	3.22	3.17	3.11×10^{-4}

The amount of electricity required to change the potential by 0.10 volt during establishment of the oxygen overvoltage, after the latter had once been attained and allowed to decay, was 2.0×10^{-5} coulombs.

Curves A and B (see fig.16) show that the depolarization due to oxygen in the solution occurrs at potentials more negative than these observed at palladium and rhodium electrodes.

Experiments were also made with iridium electrodes in N/5 sodium hydroxide. Their behaviour was similar to that in acid solution when polarized with small currents.

Unlike palladium and rhodium, iridium showed no signs of oxide formation when polarized with larger currents.

Platinum in N/5 sodium hydroxide

Some experiments were made to find out whether a depolarization process, similar to the depolarization due to reduction of oxide at palladium and rhodium electrodes, could be observed at platinum electrodes when polarized anodically with fairly large currents in alkali. It was found, however, that no oxide formation took place at a platinum electrode when thus treated.

Discussion.

The relationship between the rate of change of potential of an electrode with the polarizing current density is a simple one.

When an electrode is made anodic an excess of positive charge accumulates on the metal surface, while on the solution side an excess of negative charge will accumulate. The opposite state of affairs will hold when the electrode is made the cathode. For present purposes it is not necessary to discuss in any detail this interfacial electrial double layer and it will suffice to bear in mind that it can be represented as a simple condenser system, in that it can be charged and discharged.

If no depolarization process is taking place, i.e. electrons are neither passing from the electrode to cations in the solution nor from anions in the solution to the electrode, the whole of the current is employed in charging the condenser set up at the metal-solution interface. If the capcity of this double-layer is B, the variation of electrode potential with time is given by,

$$\frac{dV}{dt} = \frac{i}{B} \qquad (1)$$

where i is the depolarizing current. However if a depolarization process is taking place and electrons are passing across the interface at a rate i', then

the potential will change at a rate,

$$\frac{dV}{dt} = \frac{i-i'}{B} \qquad (2)$$

As i' approaches the value i, $\frac{dV}{dt}$ will approach zero and when the potential of a polarized electrode is plotted against the time from the commencement of the passage of the current any depolarization process can be observed. Obviously B has the smallest observed value of $\frac{idt}{dV}$ and for the so-called inert metals this quantity is very small. The experimental methods employed in this work are therefore delicate enough to record very small amounts of depolarization.

The behaviour of palladium, rhodium and iridium when polarized with small currents is very similar to that of platinum as described by Butler, Armstrong and Himsworth [8][10] (see p.8). With a new electrode, during the passage of the first anodic current, a considerable amount of depolarization takes place before a constant potential is attained. On allowing the oxygen overvoltage to decay and then restarting the anodic current the fall of potential is much more rapid and is governed by equation (1) above. If the electrode is now made cathodic to near the potential at which hydrogen is liberated and the current then reversed the depolarization process is again observed. This behaviour can be

readily reproduced and the linear fall of potential is probably due to the formation of a layer of adsorbed oxygen on the electrode surface. Butler, Armstrong and Himsworth found evidence of the formation of an approximately monatomic layer of adsorbed oxygen on platinum. It is possible to determine the extent of this adsorption.

Bowden and Rideal [12] consider that, when a metal electrode is cathodically polarized, the linear rise of potential to the hydrogen overvoltage of the metal is due to the deposition of hydrogen atoms on the electrode surface. They have determined the accessible area per apparent cm^2 for a number of metals. The accessible area is defined as the total area accessible to hydrogen atoms and on which they can be deposited, and it is assumed that the accessible area of a mercury surface is equal to the apparent area. They find for mercury that 6.0×10^{-7} coulombs is required to change the potential by 100 millivolts per cm^2. This value has been confirmed by Butler and Armstrong.[8] When estimating the effective areas of electrodes in this way, the electrolyte M/10 sulphuric acid, must be saturated with hydrogen and freed from the slightest trace of oxygen. In the present work no experiments were made in hydrogen saturated solutions. The effective areas were determined by comparing the values of B

(see p. 44) for palladium, rhodium and iridium with the value of B found by Butler, Armstrong and Himsworth[9] for a platinum electrode whose effective area had been previously determined by the method of Bowden and Rideal. Since the present investigation has been carried out under experimental conditions very similar to those under which Butler, Armstrong and Himsworth worked, the determination of the effective areas of palladium, rhodium and iridium by this comparitive method is justified.

The quantity of electricity passed during the linear portions of the anodic curves for palladium, and rhodium and iridium (see figs. 8,14 and 16) is approximately equal to that required for the formation of an adsorbed layer of oxygen, in which the oxygen atoms are spaced one to each metal atom. This is shown in table 14, (see p. 48).

The third column gives the quantities of electricity required to charge the double layer during the establishment of the oxygen overvoltage; this quantity gives the effective areas of the electrodes. The fifth column gives the number of atoms at one square centimetre of metal surface assuming the latter to be plane. The last column gives the quantities of electricity passed during the depolarization process, while the sixth column

Table 14.

Metal	Apparent area ($cm.^2$)	B 10^{-5} couls. per 0.1 volt	Effective area ($cm.^2$)	Atoms per $cm.^2$	Couls. for one O atom to each metal atom	Couls. passed during linear parts of anodic curves
Pt	1.0	1.0	3.0	1.6×10	16×10^{-4}	9×10^{-4}
Pd	1.0	1.8	5.4	1.7	29	30
Rh	1.0	1.2	3.6	1.7	19	9
Ir	1.0	2.0	6.0	1.7	32	22

The figures for platinum are those of Butler, Armstrong and Himsworth[9].

gives the quantities of electricity required to form an atomic layer of adsorbed oxygen. It is seen that there is good agreement between the last two columns considering the approximate nature of the calculation.

This adsorption process on platinum has been studied in detail elsewhere [9] and it is only necessary to say here that the adsorbed layer is very stable and is only removed by cathodic polarization to fairly negative potentials. Curve 3 (fig 7) was obtained when a palladium electrode, which had been anodically polarized in sulphuric acid solution, removed, washed and kept in distilled water for a period of two months, was replaced in an acid solution and anodically polarized. It is seen that the fall of potential is much more rapid than in curves 1,1 (a) and 4 thus showing that the adsorbed oxygen layer then was still present on the electrode surface. The removal of this layer on palladium during cathodic polarization commences about E_4 = + 0.90 volt and finishes about + 0.40 volt, but more negatives values of the potential are required for the removal of the adsorbed layers in rhodium and iridium. The reduction occurs simultaneously with the depolarization due to oxygen dussolved in the solution and is not readily studied owing to the masking effect of the latter depolarization.

The behaviour of these metals is similar in alkaline

solutions, but the corresponding potentials for the various processes are displaced in the negative direction. Replacing oxygen in the solution by nitrogen effects very little difference, the only result being the shortening of the cathodic depolarization due to dissolved oxygen (see curve D, fig.10.)

The third cathodic depolariztion process occurring at palladium and rhodium electrodes, at potentials more positive than the other two which occur simultaneously, must be due to the presence of some material produced during the anodic treatment. The process is not affected by the oxygen dissolved in the solution because the same behaviour is observed in solutions from which oxygen has been displaced by nitrogen. The depolarization must therefore be due to the reduction of an oxide.

There are two points to be noted at this stage. The first is that the total amount of oxide that can be produced, as measured by the quantity of electricity required to complete the cathodic depolarization, corresponds to only one molecular layer assuming its composition to be MO. The second is that the amount and rate of oxidation depend on the previous anodic treatment of the metals. The observations of the above effects are complicated by the fact that, (1) the total amount of oxide produced is so small and (2) the effect of solubility is therefore comparitively large. However most of the experiments were carried out in alkaline

solution in which the oxides were less soluble. The results are also difficult to interpret quantitatively owing to the apparent increase in the oxidisability of the electrodes with alternate oxidation and reduction. However it is possible to make a few generalisations.

Oxide formation at palladium electrodes.

It is obvious from tables 6, and 7, that the amount of oxide produced in any specific experiment is not dependent on the quantity of electricity passed during the anodic polarization in that experiment alone, but is also dependent on the previous history of the electrode. However, bearing this in mind, we can see from experiment 12, (table 6) that the greatest amount of electricity required during the cathodic process is 43.5×10^{-4} coulombs which is not much more than that required for the reduction of a monomolecular layer of Pd O (see p.48). More interesting is a comparison of the results of the several series of experiments shown in fig.17.

For each series the amount of cathodic polarization required to complete the depolarization process is plotted against the amount of anodic treatment in each experiment. Series A was made in sulphuric acid, B and C in sodium hydroxide.

From curves B and C it is obvious that, as the amount of anodic polarization in consecutive experiments increases, the amount of oxide formed at first increases to an approximately steady value, but subsequently with

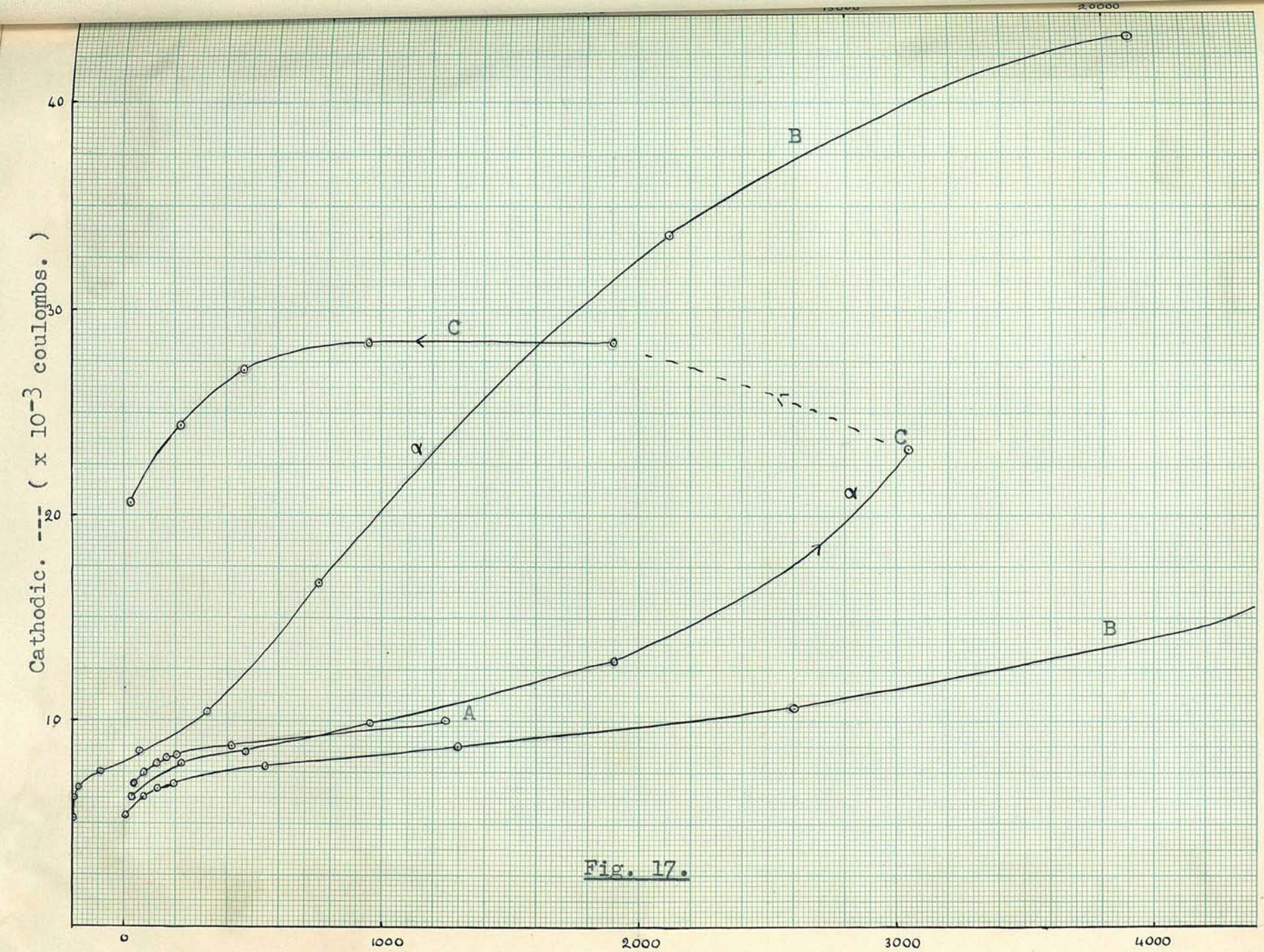

40
30
20
10
Cathodic. --- (x 10⁻³ coulombs.)
B
C
α
C
α
A
B
0
1000
2000
3000
4000
Anodic. --- Scale for curves A, B, and C. (x 10⁻³ coulombs.)

Fig. 17.

long polarizations increases again. Finally after very long polarizations very little increase, if any, in the a amount of oxidation can be detected.

The increase in the slopes of curves B and C at α must be due to the greater ease of oxidation which results from a considerable amount of anodic treatment. This accumulative effect is not produced by the anodic treatment in any given series of experiments alone but depends on the toal amount of anodic treatment given to the electrode. However the effect is greater the shorter the intervals of rest between experiments (series C followed B immediately), and disappears after the electrode has been allowed to rest for fairly long periods. That there is a limit to the extent of this effect is readily shown by the flattening out of curve B after very long anodic polarization.

The most striking fact that emerges is the hysteresis effect which is observed when the length of the anodic polarization is reduced once more. In experiment 6, series C (see p.32) 23.30×10^{-4} coulombs were required for the redution of the oxide produced during the anodic polarization with 3050×10^{-4} coulombs whereas in experiment 8, 28.30×10^{-4} coulombs were required to reduce the oxide produced by 952×10^{-4} coulombs. Taking the ratio, of the amount of electricity required for the cathodic depolarization to that passed during the anodic treatment in any one experiment, as

the effeciency of oxidation then this ratio for the last experiment in series C is 6.5%.

Oxide formation at rhodium electrodes in sodium hydroxide solution.

Very similar results to the above are obtained for oxide formation at rhodium electrodes. Continued anodic treatment also produces an increase in the oxidisability of rhodium.

It would seem from the experiments in series D and E that polarization with a high current density for a short time is more effective in producing this increase in oxidisability than a longer period of polarization with a smaller current density.

Rhodium is especially interesting in that after it has been polarized anodically with large currents oxide is formed anodically with small currents with which it was previously undetectable.

From fig.18. in which the results of table 12 are plotted it is seen that, under the above condition with small currents, the effeciency of oxidation (as defined above) soon approaches an appreciable value, ca. 50%, and ultimately falls of to a very small value. The greatest amount of electricity required to reduce the oxide formed in an experiment is 21.1×10^{-4} coulombs; this quantity is a little greater than that required to form a monomolecular

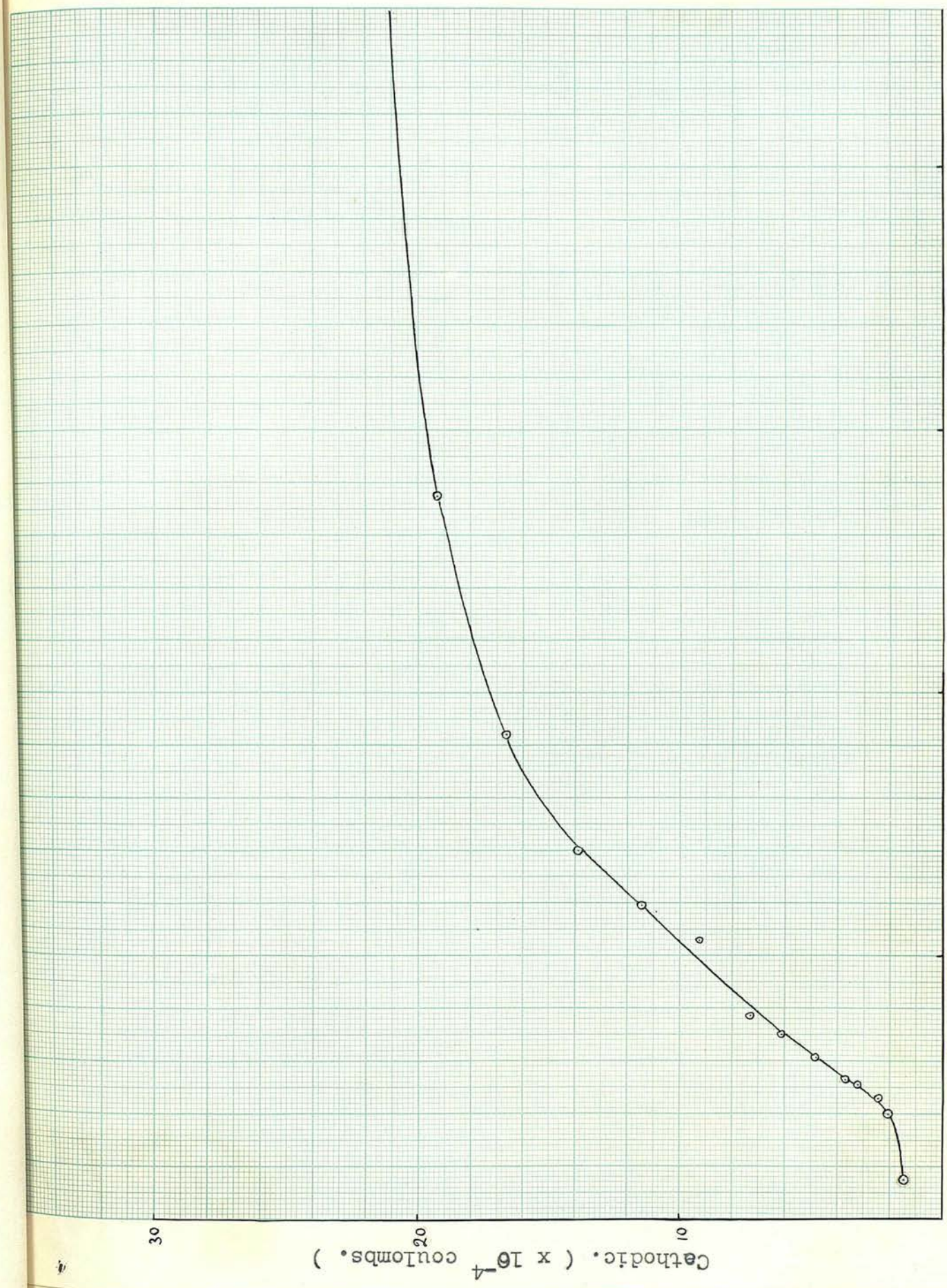

Cathodic. (x 10^{-4} coulombs.)
10
20
30
Anodic. (x 10^{-4} coulombs.)
10
20
30
40

Fig.18.

layer of oxide with the formula RhO (see table 14 p.48).

However it must be borne in mind that these quantities of definite oxides exist on the electrode surface side by side with the layer of adsorbed oxygen atoms described above. The latter layer is not removed simultaneously with the oxide, for when the electrode has been cathodically polarized to the point at which all the oxide is removed and is then made anodic with a small current, the potential falls rapidly to the oxygen potential, thus demonstrating the presence of the adsorbed oxygen layer on the electrode surface.

Although the removal of the oxide is fairly easily studied, the study of its formation is masked by the fact that it takes place simultaneously with the anodic evolution of oxygen. It is probable that the long time required for the attainment of the maximum overvoltage is accounted for by the formation of oxide. The variation of potential of a palladium electrode with time when anodically polarized in sodium hydroxide solution with a current of 540 x 10^{-6} amperes, is shown in fig.19.

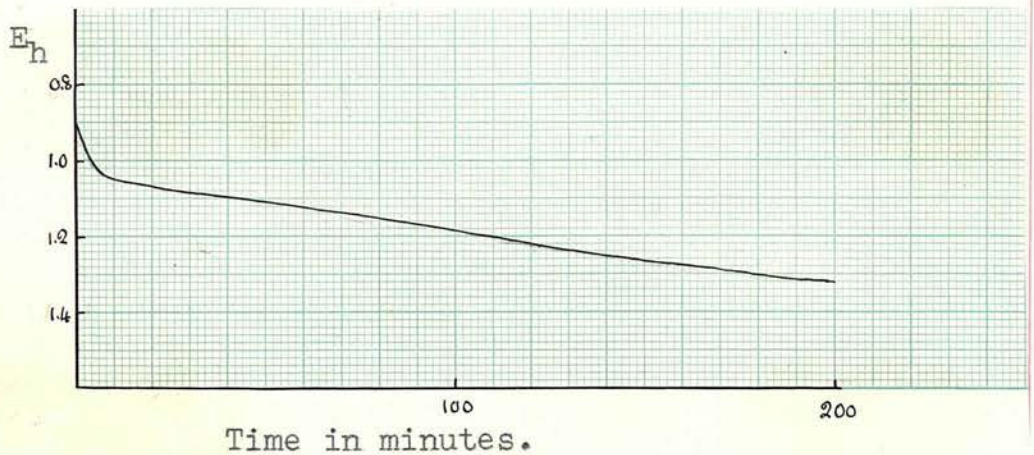


Fig.19.

The initial potential E_h = +0.92 volt corresponds to a considerable oxygen overvoltage and the change of the potential with time is almost constant. In the case of rhodium, oxide formation can take place before the oxygen potential is reached and this has already been studied.

Conclusions.

From the above considerations it is seen that when palladium, rhodium and iridium electrodes are polarized anodically an approximately monatomic layer of oxygen atoms is adsorbed on the metal surface. With very long polarizations oxide is formed at palladium and rhodium electrodes. However the amount formed is very small (not much more than a monomolecular layer with the formula MO), and is formed very slowly. Consequently no oxide formation can be detected with small anodic polarizations.

The striking hysteresis effect observed above can only be accounted for by a change in the state of the metal surface brought about by the oxidation and reduction of the electrode. It is well known that, when a metal is alternately oxidised and reduced, the surface area is increased considerably (see experiments with lead electrodes, p.). If a similar increase in surface area was effected at palladium and rhodium electrodes, then the

increasing amounts of oxide formed would be accounted for in this way. However, the greatest amount of oxidation which occurs is only of the order of one molecular layer and the reduction of a surface layer of oxide molecules could not be expected to expose more metal atoms. The approximately linear change of potential during the cathodic depolarization, due to reduction of the oxide, also demonstrates the presence of a surface film which is no more than one molecule thick. The depolarizing current i' (p.44), which is the rate of transfer of electrons from the electrode to oxide on the surface, is governed by an equation of the type (8),

$$i' = kce^{V}$$

where c is the effective concentration of depolarizer at theelectrode. With the small currents employed in this work, once i' has approached the the value of i it will remain practically equal to it. However if c decreases then V must increase in order to maintain the value of i' equal to the polarizing current. The linear change of potential during the reduction of the oxide is then due to the decrease in the concentration of the depolarizer at the electrode with time.

Moreover, no change in the capacity B (p.44) of the electrodes could be detected after the completion of the above experiments, thus showing conclusively that no increase in the surface area

of the electrodes had been brought about by the alternate oxidation and reduction.

The observed hysteresis effect must therefore be attributed to a change in the state of the surface after long anodic polarization, whereby oxygen atoms are more readily adsorbed with the subsequent formation of a definite oxide. A change in the spacings of the surface atoms would probably account for this increase in oxidisability.

After rhodium has been polarized with large anodic currents, the state of the surface is such that when the electrode is now polarized with small anodic currents, oxide is formed simultaneously with the adsorption of oxygen at potentials less negative than the oxygen potential.

Summary

(1) (a) A study has been made of the anodic and cathodic polarization of palladium (p.19-p.24), rhodium (p.33-p.34), and iridium (p.41-p.42) electrodes in dilute sulphuric acid, with current densities between 1 and 50 microamps.

(b) It is found that an approximately monatomic layer of adsorbed oxygen is formed at these electrodes during anodic polarization, at potentials less positive than that required for the liberation of oxygen. (p.46-p.48).

(2) (a) A study has been made of the electrochemical behaviour of palladium (p.29-p.32), rhodium (p.35-p.40), iridium (p.42) and platinum (p.43), in dilute sodium hydroxide, with current densities between 100 and1000 microamps.

(b) There is substantial evidence of oxide formation at palladium and rhodium electrodes when anodically polarized with these larger currents. (p.51-p.57).

(3) (a) The amount formed is small; not much more than one molecular layer.

(b) It is formed very slowly, and probably results from interaction between adsorbed oxygen atoms and metal atoms.

(c) A striking increase in the oxidisability

of the electrodes, is noted after long anodic polarizations. This is brought about by a change in the forces existing between the metal atoms at the electrode surface. The effect is especially marked in the case of rhodium where oxidation occurs with small currents, with which it previously could not be detected, after such long anodic polarizations.

Part II.

(A) Electrochemical behaviour of nickel and iron in N/5 sodium hydroxide.

(B) Electrochemical behaviour of lead in M/10 sulphuric acid.

(A) Introduction.

Nickel and iron are perhaps two of the most easily passified of the more common metals. When made anodic, even with very small currents in alkaline solution, both metals are very inert and the potential at which oxygen is freely evolved is rapidly attained. However with continued anodic polarization oxide formation takes place and this has been the basis of a great deal of research owing to the importance of these metals in the Edison cell.

The electrochemical system of the charged Edison accumulator is,

$$\overset{+}{Ni(OH)_3} \,|\, \text{concentrated KOH} \,|\, \overset{-}{Fe}$$

and that of the discharged cell,

$$Ni(OH)_2 \,|\, \text{concentrated KOH} \,|\, Fe(OH)_2$$

Although the hydroxides are hydrated and the extent of this hydration is not readily determined, the cell reaction taking place during charge and discharge can be represented by the equation:

$$2\,Ni(OH)_3 + Fe \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,Ni(OH)_2 + Fe(OH)_2 \quad .$$

Foerster(11), among others, has made extensive studies of the reactions taking place at both electrodes.

His electrolyte was 2.8N.KOH (i.e. somewhat more dilute than that used in the working cell, 3.8N.KOH). He found that a freshly charged nickel

oxide electrode shows an initial potential in this solution of E_h = +0.60 volt. On standing this falls rapidly at first and then more slowly, till after some weeks it reaches the value +0.47 volt, where it remains constant. This potential represents the equilibrium potential of hydrated nickel sesquioxide. If the freshly charged plate be discharged, the course of the potential changes with time is similar to that shown by the plate on standing. There is an initial rapid fall, followed by a long discharge during which the potential, though slowly dropping, is almost constant, and about 0.04 volt lower than the equilibrium value for the hydrated Ni_2O_3. Finally it drops rapidly, and there is a second short halt at about -0.10 volt. On charging the positive plate, the potential falls rapidly and then more slowly to +0.65 volt.

Foerster's explanation of these observations is that the first process taking place at the anode is the discharge of hydroxyl ion which at once combines with the depolarizer present, NiO. The higher oxidation product is assumed to be the peroxide NiO_2 which then reacts chemically according to the equation,

$$NiO_2 + NiO \longrightarrow Ni_2O_3$$

so that the sesquioxide results from a secondary purely chemical reaction. The result of anodic polarization is therefore to produce a solid solution

of NiO, Ni_2O_3 and NiO_2, the proportions of the latter two oxides gradually increasing. Nickel peroxide is unstable and rapidly decomposes into the sesquioxide and free oxygen, only the fact that it is dissolved in the two lower oxides lends it a greater degree of stability. The final result after charging will be that most of the active mass will contain all its nickel as Ni_2O_3 with a little NiO_2, but after some time has elapsed and the oxide system has reached a state of equilibrium the nickel will all be present as Ni_2O_3.

Foerster attributes the short halt at -0.10 volt to some other oxide produced during the decomposition of the NiO_2.

It is well known that finely divided iron is, under ordinary conditions, passive in alkaline solution. However, if it is cathodically charged with hydrogen it becomes active, showing a potential in 2.85N.KOH of -0.87 volt. It will now readily dissolve anodically and Foerster and Herold[13] have shown that the electrode process is

$$Fe \longrightarrow Fe^{++} + 2\epsilon \qquad (1)$$

the product being ferrous hydroxide.

The above lends support to Foerster's well-known views on the passivity of iron and similar metals, namely, that when pure, these metals are passive and only become active when they have received a charge of hydrogen, the degree of activity

corresponding to the concentration of the hydrogen.

This anodic polarization decreases the hydrogen concentration by causing the dissolved hydrogen to ionise, thus making the potential more and more noble. Finally, when the limit of -0.75 volt is reached, passivity sets in and the iron no longer dissolves as Fe^{++} ions: Another process now sets in - viz.

$$Fe^{++} \longrightarrow Fe^{+++} + \epsilon \qquad (2)$$

involving the transformation of ferrous into ferric hydroxide. The second discharge stage is never reached under normal working conditions in the Edison accumulator. On charging, (1) is not reversed owing to the fact that the adsorbed hydrogen makes the iron less passive and thus a more negative value of the potential is necessary for deposition of metallic iron. The potential required is about -1.10 volt. However, it must be remembered that these experiments have been made with substances in a very fine state of division (as is required in the Edison cell), and thus would be expected to show oxidation and reduction changes more readily than the metals in bulk.

Experiments with nickel and iron electrodes in N/5 sodium hydroxide have been made.

Experiments with nickel in N/5 sodium hydroxide.

No depolarization, similar to that shown by platinum, palladium, rhodium and iridium electrodes, is observed when a nickel anode is polarized. This is probably due to the presence of a protective air-adsorbed oxygen or oxide film and although this may be removed during the cathodic depolarization due to oxygen in the solution (occurring at E_h = -0.10 volt), its study is complicated by the adsorption of hydrogen deposited during the cathodic polarization. This hydrogen is removed during the subsequent anodic polarization.

However oxidation readily occurs at a nickel anode even with small currents, as shown below.

The following changes in potential were observed after an electrode had been made anodic for some time with 195 microamps., and was then cathodically polarized with a current of 8.8 microamps. The potential rose rapidly from the oxygen overvoltage at E_h = +0.90 volt, remained constant at about +0.60 volt for a considerable time depending on the amount of the previous anodic polarization, and then rose rapidly to -0.10 volt at which oxygen in the solution acted as a depolarizer. The depolarization due to reduction of oxide is very clearly defined

as can be seen from fig.1 , in which the curves 1, 2, and 3 and 4 were obtained with a cathodic current of 8.8 microamps. after the electrode had been anodically polarized for 3, 30, 60 and 3 minutes respectively with a current of 195 microamps.

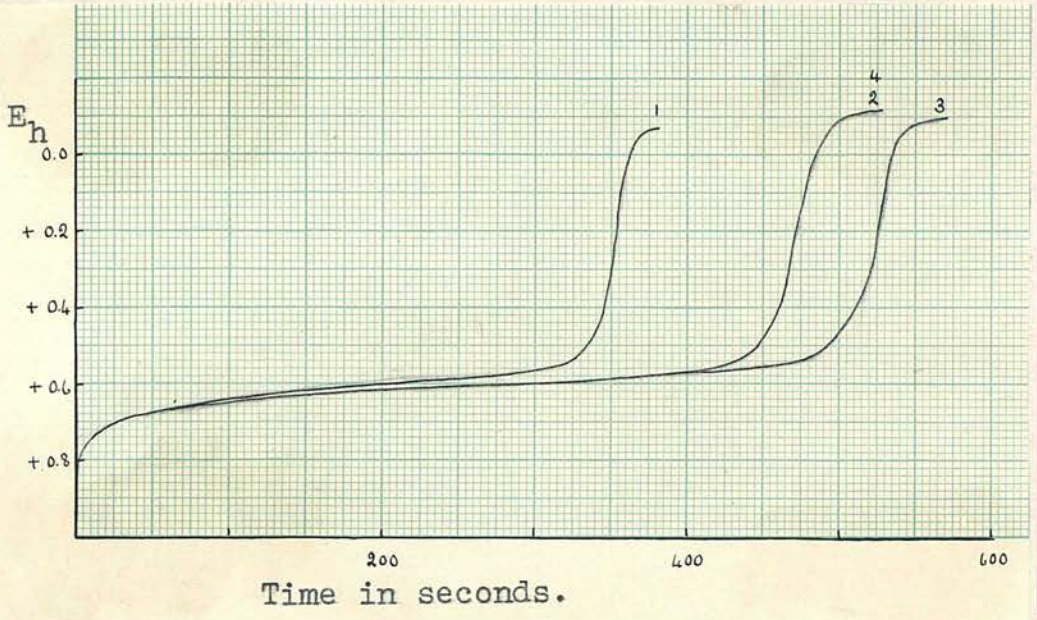


Fig. 1 .

The solubility of the oxide was now studied. The oxide is somewhat soluble in alkali as the following experiments show. The electrode was made anodic with a current of 500 microamps. for 3 minutes and the effect of an interval on the time required to reach +0.08 volt, when the electrode had been made cathodic with i = 110 microamps., observed. The results are given in table 1 .

Table 1.

Experiment	Interval	Time to reach +0.08 volt
1	0 mins.	50 seconds
2	5 "	43 "
3	10 "	44 "
4	7 " (stirring)	45 "
5	39 mins.	38 "
6	180 "	24 "

Effect of previous anodic treatment on oxide formation.

From fig. 1 it is obvious that nickel, as well as the other metals previously studied, shows a considerable increase in its oxidisability after anodic polarizations. This effect is well demonstrated in table 2 (p.66) which gives the results of a series of experiments (see figs. 2, 3 and 4, p. 67) in which the electrode was made anodic with a current of 190 microamps. for short times (30 seconds) up to long times (660 minutes) and back again to short times. The oxide formed during these experiments was reduced with a current of 8.4 microamps.

Table 2.

Expt.	Anodic coulombs	Cathodic coulombs to +0.08 volt	Expt.	Anodic coulombs	Cathodic coulombs to +0.08 volt
1	5.7×10^{-3}	2.62×10^{-3}	20	5.7×10^{-3}	5.70×10^{-3}
2	11.4	3.88	19	11.4	7.14
3	22.8	5.00	18	22.8	7.62
4	45.6	5.84	17	45.6	8.20
5	91.2	6.32	16	102.6	8.70
6	182.4	6.70	15	182.4	8.85
7	364.8	7.04	14	399.0	9.00
8	729.6	7.32	13	741.0	9.05
9	1368.0	7.78	12	1368.0	9.18
10	2736.0	8.20			
11	7524.0	9.12			

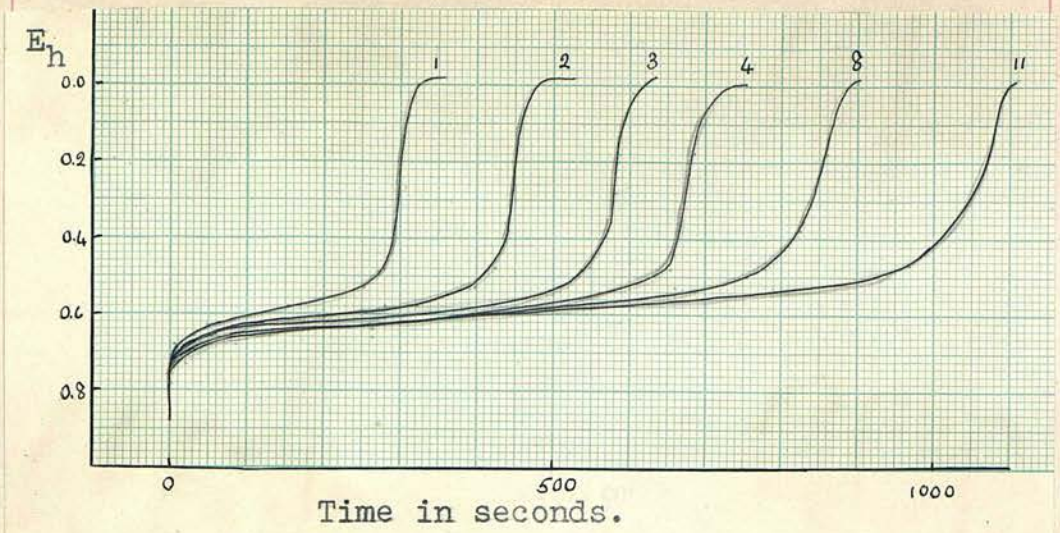


Fig.2.

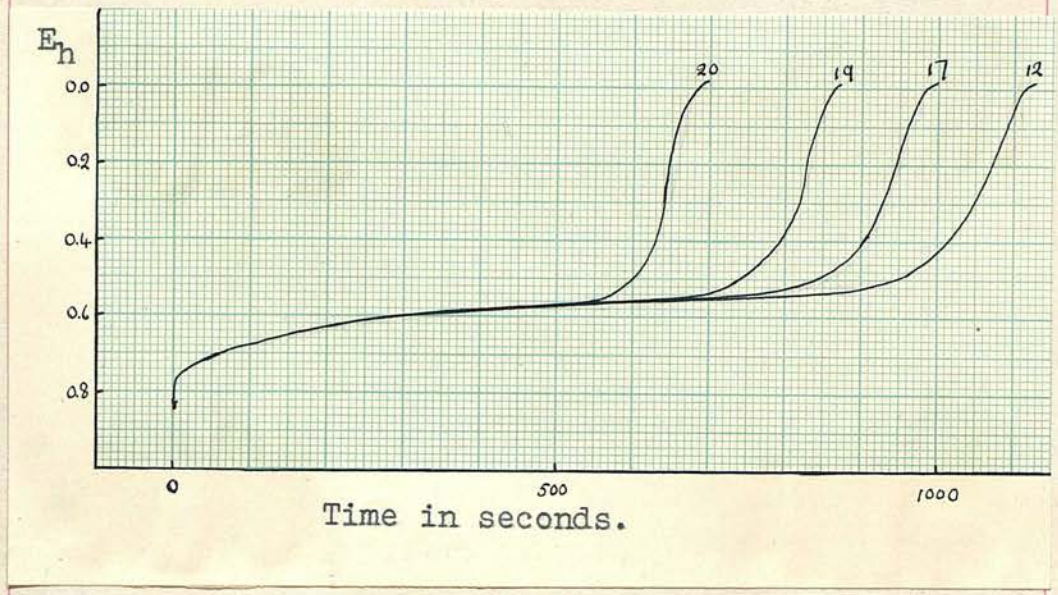


Fig.3.

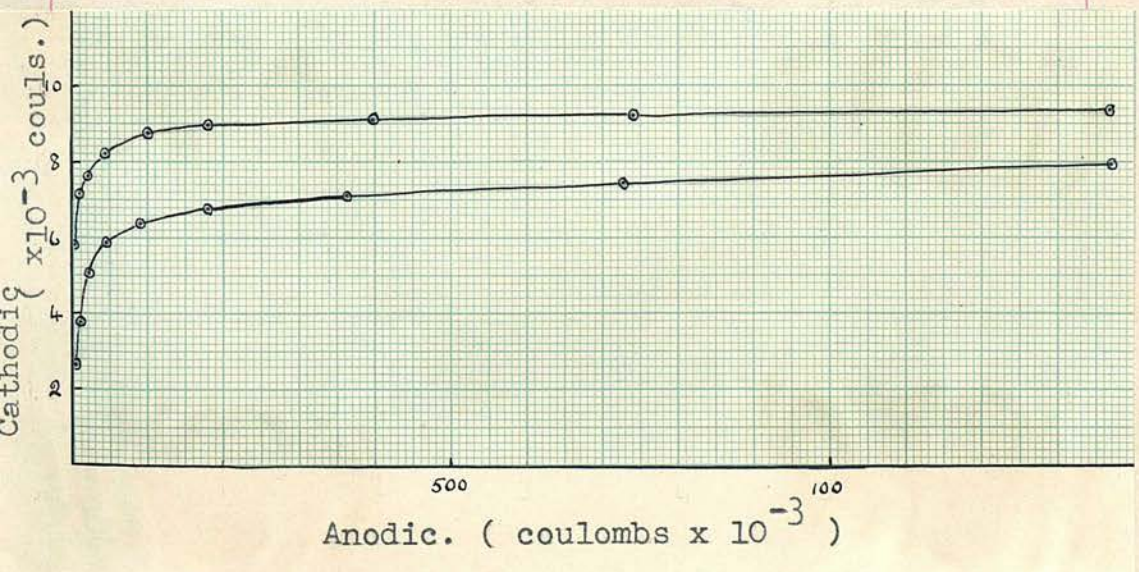


Fig.4.

Oxidation at nickel anodes can be effected with smaller currents. The results of a series of experiments in which both anodic and cathodic currents were the same, 24.8 microamps., are shown in table 3 .

Table 3.

Experiment	Anodic coulombs	Cathodic coulombs to +0.08 volt
1	7.44×10^{-4}	4.99×10^{-4}
2	14.88	8.68
3	29.76	27.80
4	59.52	52.10
5	119.04	75.40
Electrode rested for a few days		
6	7.44	5.94
7	14.88	9.65
8	119.04	64.00

Although the electrode received equal amounts of anodic polarization in both experiments 5 and 8, the amount of oxidation which takes place in the latter is considerably less than in the former. This is due to the smaller amount of anodic treatment which the electrode had received immediately prior to 8 compared with that received immediately prior to 5.

The behaviour of a nickel electrode which had been cleaned in aqua-regia, and whose surface had a roughened appearance, was very similar to the above. The amount of oxide formed in corresponding experiments was practically the same.

Some experiments were made on electrodes which had been heated until they had acquired a bluish film of oxide on their surface. On cathodic polarization no reduction of oxide took place, but electrochemical oxidation took place at the electrodes when anodically polarized. From table 4 it is evident that a greater amount of oxidation takes place at an oxide covered electrode. This may possibly be due to an increase in area of the metal brought about by the heat treatment in air although a considerable amount of the new surface must be covered with a fairly thick oxide film. An hysteresis effect is also observed here, (compare experiments 7 and 12).

Similar behaviour was shown by several electrodes treated in the above manner. However one electrode was quite inert and oxygen did not act as a cathodic depolarizer at the oxide covered surface. It is possible that this oxide film was in a very good state of repair [14] thus covering completely the whole surface.

Table 4.

Expt.	Anodic Coulombs		Cathodic Coulombs to +0.08 volt.
1	i = 26.6 microamps.	0.80×10^{-3}	0.32×10^{-3}
2		1.60	0.75
3		3.20	1.46
4		6.40	2.66
5		12.80	5.30
6		28.80	12. 20
7	i = 200 microamps.	48.0	21.00
8		96.0	37.20
9		192.0	46.00
10		384.0	57.00
11		1704.0	68.00
12		48.0	39.80

Iron in N/5 sodium hydroxide

It is well known that iron like nickel is completely passive in alkaline solution and therefore it was decided to examine iron in the above manner for any signs of oxidation. The electrodes were made of purest electrolytically prepared iron and before use were polished with fine emery.

When such an electrode was first anodically polarized the potential fell linearly with time from the equilibrium potential of the electrode in this solution (E_h = -0.1 volt) to E_h = +0.80 volt. After this depolarization process had taken place the electrode was quite inert when polarized with a large number of current densities. Oxygen dissolved in this solution acted as a cathodic depolarizer in the region of -0.30 volt. However if the potential was made negative to the neighbourhood of the deposition of hydrogen, then a similar depolarization process was observed when the electrode was again made the anode. This behaviour was independent of the gas dissolved in the electrolyte and is evidently due to the removal of hydrogen which is adsorbed on the electrode surface during the cathodic polarization. The first anodic depolarization is probably accounted for by the fact

that almost all iron produced electrolytically contains hydrogen which is deposited along with the metal.

Hydrogen is adsorbed at an iron cathode in N/5 sodium hydroxide at potentials which are less negative than that required for the reversible deposition of hydrogen in this solution (E_h=-0.80 volt). In table 5 are shown the results of a series of experiments (see fig. 5) in which the electrode was made cathodic to increasingly negative potentials, the current was then reversed and the time required to reach +0.68 volt noted. The solution was saturated with nitrogen thus allowing high negative potentials to be readily obtained with the small current used, 9.8 microamps.

Table 5.

Expt.	potential reached	cathodic coulombs	anodic coulombs to reach +0.78 volt.
1	-0.22 volt	1.47×10^{-4}	1.28×10^{-4}
2	-0.32	2.45	1.76
3	-0.42	4.60	2.85
4	-0.47	6.57	3.72
5	-0.52	11.80	5.40
6	-0.57	19.20	10.40
7	-0.62	28.40	15.80
8	-0.72	62.60	47.00
9	-0.72	62.60	46.00

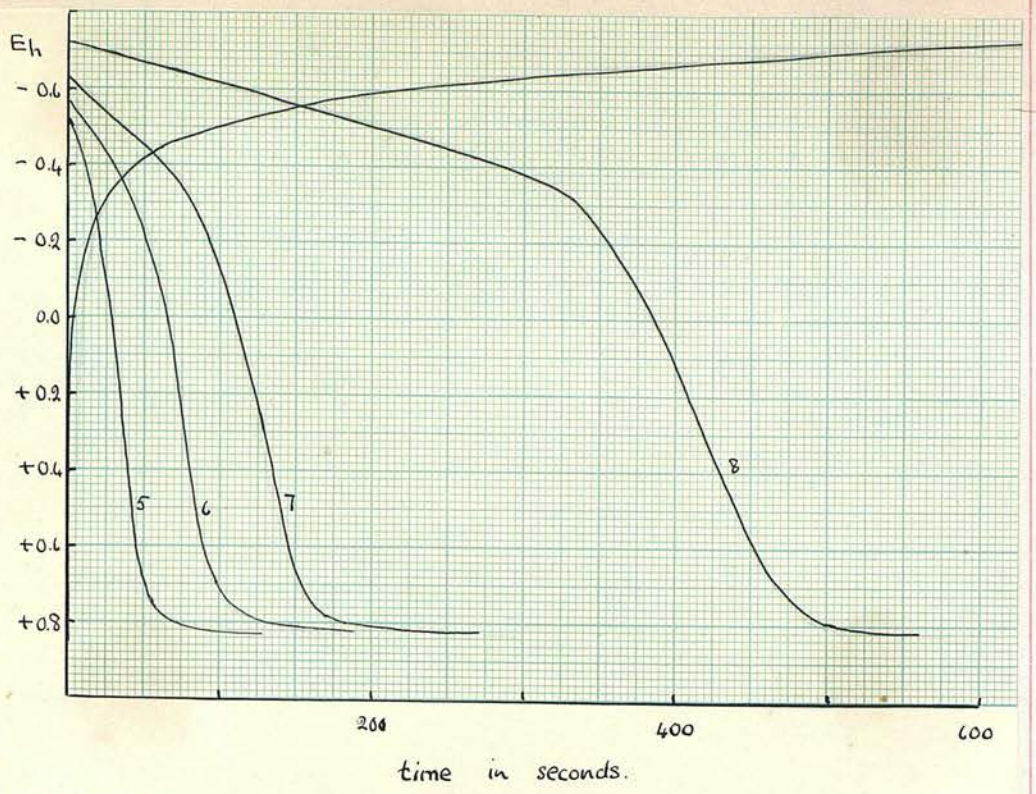


Fig.5.

Experiments 8 and 9 show that this behaviour is readily reproduced. The quantities in the last column for the later experiments are greater than those required to change the potential of the electrode when no depolarization process is taking place, for when the latter state of affairs exists $\frac{idt}{dV}$ during the passing of anodic current is 1.73×10^{-5} coulombs / 0.10 volt. Up to experiment 3 very little, if any, adsorption of hydrogen occurs during the cathodic process but in later experiments this takes place to considerable extent depending on the amount of polarization. Roughly speaking the quantities in the last column are just a little over one half of

those in the third, and this margin increases with the increasing time of the experiment. This may be due to the rate of solution of adsorbed hydrogen into the solution being just one half the rate of the deposition of hydrogen with this particular current density. The increase in the ratio anodic / cathodic in later experiments would then be accounted for by the increasing concentration of hydrogen in the vicinity of the electrode.

An iron electrode covered with a thin black oxide film showed similar behaviour in alkali, and no sign of reduction of the oxide was shown.

Discussion.

Oxide formation at nickel electrodes.

When a new nickel anode is first polarized the fall of potential to the oxygen overvoltage is fairly rapid; the quantity of electricity required per 0.10 volt is 2.10×10^{-5} coulombs. When the overvoltage is allowed to decay, the same quantity is required to re-establish it.

When the current is reversed after an anodic polarization (in oxygen saturated solution) a marked depolarization process at $E_h = +0.60$ volt is observed, and another at $E_h = -0.10$ volt.
The first depolarization depends on the amount of anodic polarization which the electrode has received and is also observed in nitrogen saturated solution, whereas the latter depolarization is independent of the anodic treatment and is not observed in solutions freed from oxygen. The depolarization process observed at the more negative potentials is due to the ionisation of oxygen dissolved in the electrolyte and corresponds to that observed at the other electrodes examined.

There is little doubt that the lower cathodic break is due to the reduction of an oxide, which is slightly soluble in alkali (see table 1).

It is now necessary to determine which oxide is

formed during the anodic polarization and what is the reduction product. The depolarization process begins about +0.67 volt and finishes about +0.47 volt. This process is in the neighbourhood of that observed by Foerster for the discharge of the positive plate of an Edison cell. The reaction is

$$Ni_2O_3 + H_2O + 2\epsilon \longrightarrow 2\ NiO + 2\ OH',$$

and the lower cathodic break observed in this work must be due to the reduction of Ni_2O_3, formed during the anodic polarization, to NiO. Nickel monoxide is not reduced until much more negative potentials are attained and in fact the study of its removal is masked by the hydrogen liberation which then takes place.

The behaviour of a new nickel electrode on anodic polarization can be explained in the following way. The rapid fall of potential to the oxygen overvoltage is due to the existence on the electrode surface of a film of the monoxide. Simultaneously with the evolution of oxygen, this monoxide is oxidised to the sesquioxide; if any peroxide is formed it is so unstable that its presence cannot be definitely recorded. During the subsequent cathodic polarization the Ni_2O_3 is reduced to NiO, and only when the electrode is made cathodic to the potential at which hydrogen is liberated, is the monoxide reduced to metal. Once the monoxide has been reduced, the subsequent anodic curves show a

depolarization process similar to that observed in the case of palladium and similar metals. This process starts at -0.05 volt and finishes at +0.65 volt during which the change of potential is almost linear and 3.4×10^{-3} coulombs are passed. A com-parison of the quantity of electricity required to establish the oxygen overvoltage at a nickel electrode, with those required for the other metals(see p.48), gives the effective area of a nickel electrode as 2.10 times its apparent area ($1cm.^2$). It can then be calculated that 4.36×10^{-3} coulombs are necessary to form a monomolecular oxide layer in which the oxygen atoms are spaced one to each nickel atom.

During anodic polarization therefore a monatomic adsorbed oxygen layer, similar to those on palladium, platinum, rhodium and iridium, is formed. However the forces between the adsorbed oxygen atoms and the metal atoms are sufficiently strong to enable a definite oxide NiO to be formed which is then oxidised to the sesquioxide, at higher potentials.

The initial behaviour of a new nickel anode shows that the attractive forces between nickel and oxygen are sufficiently great to form an approximately monomolecular layer of oxide NiO in air.

Nickel also shows a hysteresis effect similar to that exhibited by palladium and rhodium. This is well shown in table 2 . The greatest amount of Ni_2O_3 formed on a nickel electrode is recorded in experiment 12

(table 2), where 9.18×10^{-3} coulombs are required to reduce the Ni_2O_3 to the monoxide; this quantity is not much more than would be required to reduce three or four molecular layers of Ni_2O_3 to NiO.

The experiments with the oxide covered electrodes gave similar results, but it is evident, from table 4 p. 70 , that a great amount of oxidation occurs at such electrodes. In experiment 11 the quantity of cathodic electricity required, would be sufficient to reduce a layer 30 molecules thick. No doubt this increase in the surface area of the electrodes, brought about by the heat treatment in air, is responsible for the increased amount of oxidation. The hysteresiseffect here is more marked owing to the appreciable increases in surface area brought about by the alternate oxidation and reduction of such a thick oxide film. The efficiency of oxidation of this air-acquired film of NiO to Ni_2O_3 is fairly high.

The short depolarization observed by Foerster at -0.10 volt is probably due to oxygen, resulting from the decomposition of NiO_2, occluded in the porous mass. This is similar to the depolarization, due to oxygen dissolved in the electrolyte, observed in this work.

Iron in N/5 sodium hydroxide.

The results of the experiments with iron show no indication of any oxidation or reduction of oxide. The only depolarization effect observed, other than that due to oxygen in the solution, is the ionisation of hydrogen during anodic polarization after the electrode has been made cathodic to fairly negative potentials. Foerster's observation that solution of hydrogen in the metal renders it active is not supported by the above experiments. However, it must be remembered that he worked with finely divided iron, and it is well-known that any metal in such a state is much more active than the metal in bulk (see experiments with lead, p. 84).

It must be assumed that the iron from which the electrodes were prepared had already acquired a protective oxide film[14], which prevented further oxidation by electrochemical methods, although hydrogen ions were able to penetrate this film with comparative ease.

(B) Introduction

The electrochemical behaviour of lead has been studied in great detail, owing to the importance ofthe metal in the construction of the lead storage battery.

The charged cell can be represented thus:

$$\overset{+}{PbO_2}\,|\,H_2SO_4\,|\,\overset{-}{Pb}$$

and the discharged cell by,

$$PbSO_4\,|\,H_2SO_4\,|\,PbSO_4$$

The reactions taking place during discharge and charge are readily explained on the basis of the well-known "double sulphate theory" of Gladstone and Tribe. During discharge these reactions are:

At the positive electrode,

$$PbO_2 \longrightarrow Pb^{++++} + 2\,O^{"}$$
$$Pb^{++++} + 2\epsilon \longrightarrow Pb^{++}$$
$$Pb^{++} + SO_4^{"} \longrightarrow PbSO_4$$
$$4\,H^{+} + 2\,O^{"} \longrightarrow 2\,H_2O$$

At the negative electrode,

$$Pb \longrightarrow Pb^{++} + 2\epsilon$$
$$Pb^{++} + SO_4^{"} \longrightarrow PbSO_4$$

The reverse processes take place when the cell is charged, so that the total reactions are,

$$Pb + PbO_2 + 2\,H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,PbSO_4 + 2\,H_2O$$

In the original Planté process for the manufacture of accumulator plates, a current was passed between two lead plates in dilute sulphuric acid; the current was frequently reversed. In this way each plate alternately acquired a thin film of lead peroxide and was then reduced to spongy lead. No lead sulphate could be detected as an intermediate oxidation product. This was explained by the passage into solution of plumbous ions which were immediately precipitated as lead sulphate, which then began to form a non-conducting insoluble film on the electrode surface, thus increasing the effective current density to a value with which more positive potentials were rapidly attained. At these high positive potentials lead dissolves as plumbic ions with the subsequent precipitation of lead peroxide.

It was thought that a study of lead, by the methods previously described in this work, would yield results which might give an insight into the various processes occurring during the change from the metal to the highest oxidation product, and also during the reverse change.

Lead in M/10 sulphuric acid.

The lead electrodes were made from B.D.H. "Analytical reagent" product, in the usual manner. Lead is not so inert as the other metals studied and consequently its electrochemical behaviour is more complicated.

Generally a lead electrode behaved in the following way when anodically polarized. The equilibrium potential of a lead electrode in oxygen saturated M/10 sulphuric acid is E_h = - 0.27 volt. When a small anodic current (c a.10 microamps) is passed the potential is displaced from the equilibrium value by a small amount and remains there for a short time, before it falls to much more positive values, about +1.7 volt, where it remains constant and oxygen is evolved. It is obvious that a small amount of lead dissolves as plumbous ions forming lead sulphate, the potential then falls to the oxygen overvoltage with dissolution of lead as plumbic ions and evolution of oxygen. That lead peroxide is formed at these high positive potentials is shown by a depolarization process occurring at E_h = + 1.45 volt when the electrode is made cathodic. This can only be due to the transformation of lead peroxide into lead sulphate, and the latter is then reduced to metallic lead at the Pb ++ = Pb potential.

The behaviour of lead with larger current densities

is similar to that with smaller currents. It now appears that no detectable amount of sulphate is formed during the anodic process. That the peroxide formed at more positive potentials is reduced to sulphate is shown by the curves in fig. 6, where curves 1,2,3, and 4, were obtained with a cathodic current of 150 microamps. after anodic polarization with the same current for 4,8, 20 and 70 minutes respectively.

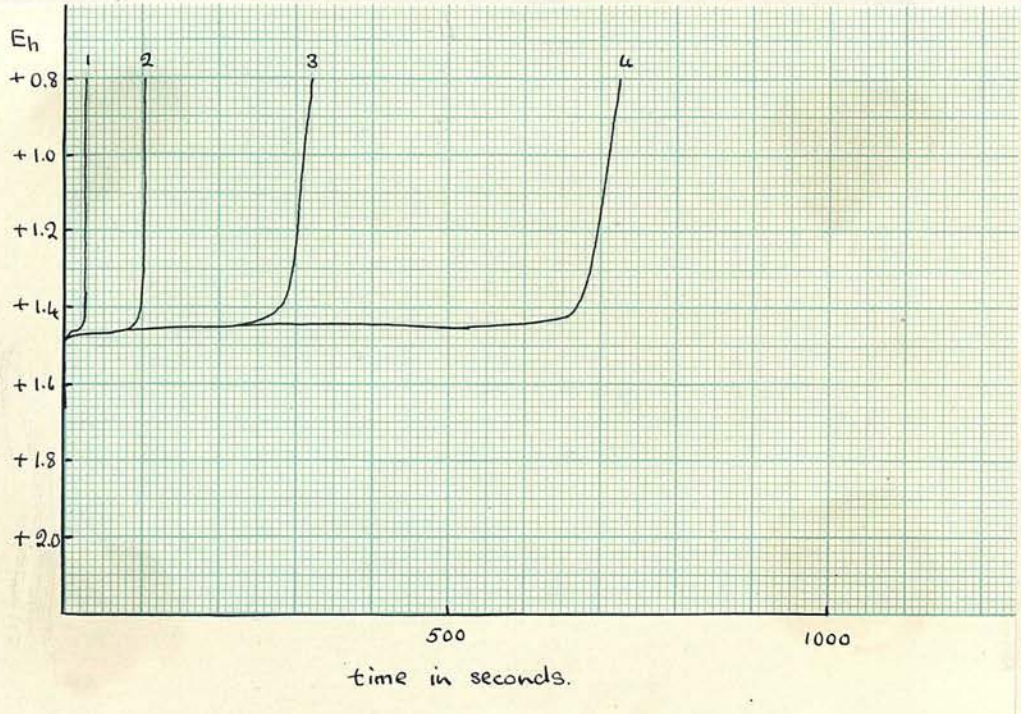


Fig.6.

The whole of the peroxide, which forms a visible film on the electrode is not reduced to sulphate during this process, for after long anodic polarization it can

still be seen on the electrode at potentials near the hydrogen liberation potential where it is ultimately reduced to metallic lead. This is accounted for by the comparatively great thickness of the film which thus prevents the outer layers of the peroxide coming into electrical contact with the metallic electrode, and only those moleculars of the peroxide which are nearest the electrode can be reduced to sulphate.

The most remarkable thing about lead is that the alternate oxidation to peroxide and reduction to metallic lead produces a surface film of lead which is in a more active condition than the metal in bulk. Once the metal is in this active form a considerable amount of it dissolves in the plumbous form on making the electrode anodic. The anodic and cathodic behaviour of an electrode in this state when polarized with a current of 1.02 milliamps. is shown in fig.7, (a) and (b). (a) shows the course of the cathodic curves from high positive potentials; the depolarization process at α is due to the reaction,

$$PbO_2 + SO_4'' + 4H^+ + 2\epsilon \longrightarrow PbSO_4 + 2H_2O \qquad (1)$$

and that at β to,

$$PbSO_4 + 2\epsilon \longrightarrow Pb + SO_4'' \qquad (2)$$

(b) gives some of the anodic curves obtained after those in (a); the numbers on the curves refer to the order in which the experiments were made. The depolarization at γ is due to the solution of lead,

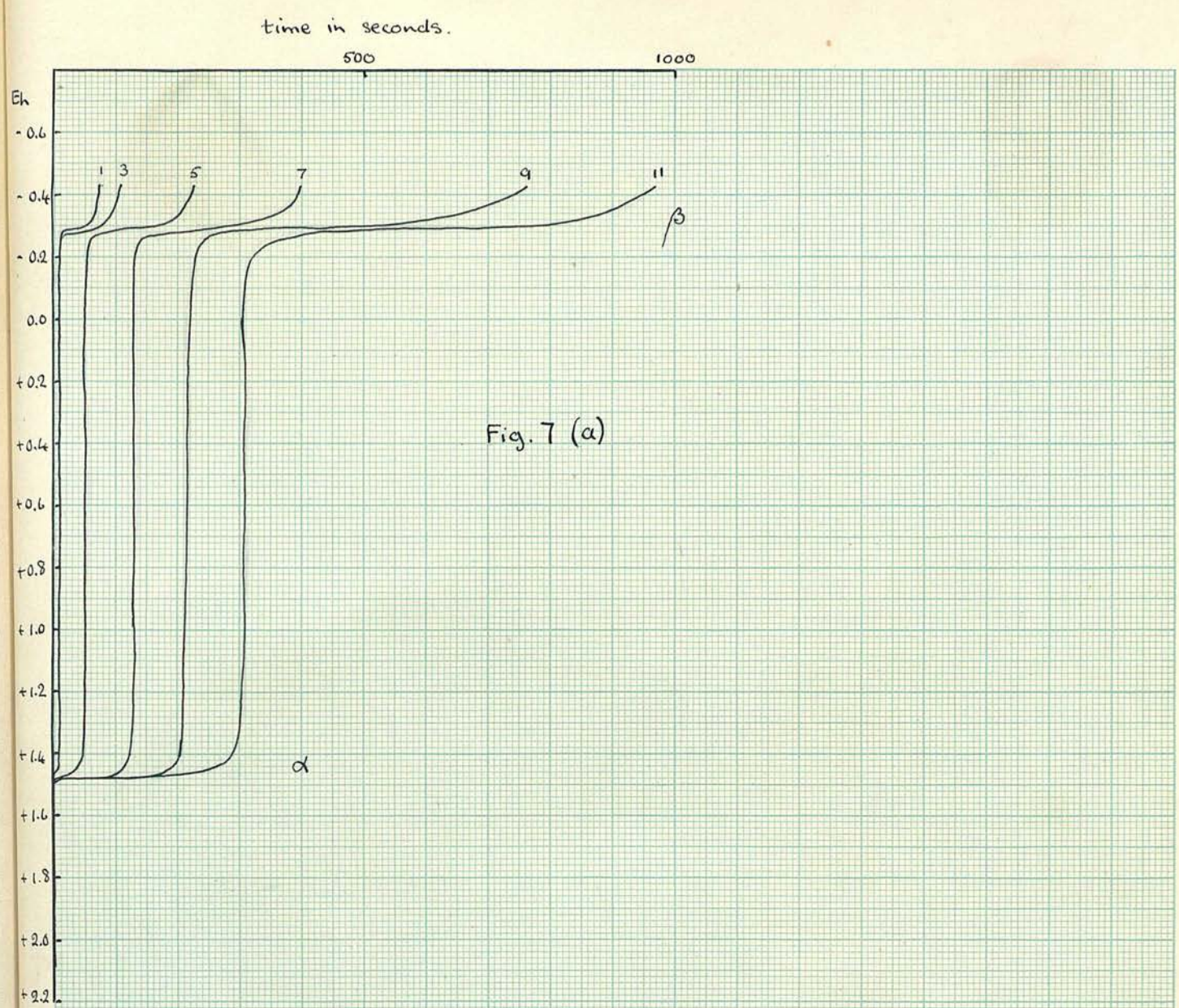

time in seconds.
500
1000
Eh
- 0.6
- 0.4
- 0.2
0.0
+ 0.2
+ 0.4
+ 0.6
+ 0.8
+ 1.0
+ 1.2
+ 1.4
+ 1.6
+ 1.8
+ 2.0
+ 2.2
1
3
5
7
9
11
β
α

Fig. 7 (a)

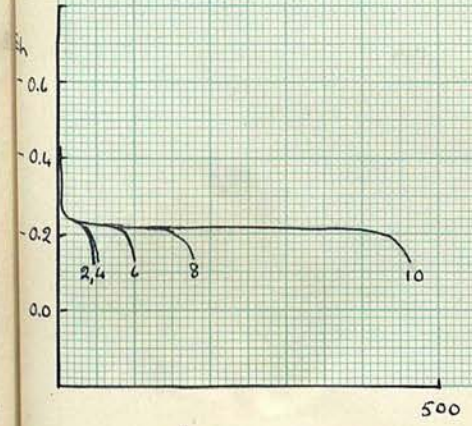

Eh
- 0.6
- 0.4
- 0.2
0.0
2,4
6
8
10
γ
500
time in seconds.

Fig. 7 (b)

$$Pb + SO_4'' \rightarrow PbSO_4 + 2\epsilon \qquad (3)$$

The length of γ increases with increasing length of β while both are always greater than α.

During anodic polarization, no depolarization process, is observed for the reverse of (1) at potentials less negative than that at which oxygen is liberated, and it is fairly safe to assume that any sulphate present on the electrode is oxidised to peroxide together with the direct production of peroxide from the metal. It would then be expected that the amount of lead deposited during β would be equivalent to the amount of PbO_2 reduced to $PbSO_4$ during α. That this is not so is seen from table 6, where the number of coulombs for each stage in the experiments are tabulated.

Table 6 .

Experiment	Coulombs x 10^{-3}		
	α	β	γ
1	7.2	69.4	
2			53.1
3	16.4	86.9	
4			56.1
5	56.1	163.6	
6			111.4
7	132.8	255.0	
8			188.0
9	215.0	541.0	
10			486.0
11	408.0	654.0	

A study of the process $PbO_2 \longrightarrow PbSO_4$ soon showed that it was by no means reversible and only a fraction of the PbO_2 was converted into $PbSO_4$, the remainder being reduced by hydrogen liberated cathodically. However, the two processes γ and β, occurring at E_h = -0.30 volt and representing the solution and deposition of lead, were studied in greater detail.

Experiments were made with an electrode which had been oxidised to PbO_2 and then reduced until a layer of active lead had been produced on the surface.

When such an electrode had been made anodic to -0.13 volt i.e. had acquired a surface film of sulphate, was then cathodically polarized to some value of the potential on the transition stage, $Pb^{++} \longrightarrow Pb$, and again made anodic to -0.13 volt, it was found that the quantity of electricity passed during this last anodic polarization was equal to that passed during the cathodic. When only a small quantity of electricity was required to complete the change the reverse also held. That is, the process $Pb \longrightarrow Pb^{++}$ was reversible.

After alternate oxidation and reduction has caused the active layer to attain a thickness corresponding to a number of molecular layers, its behaviour is somewhat different. The amount of lead which goes into solution anodically is still dependent

on the amount which has been deposited cathodically, but more negative potentials are now required to deposit the whole of the lead in the layer of sulphate. Table 7. gives the results of a few experiments made with a current of 6.5 milliamps. per cm.^{2} on such an electrode. The second column gives the number of seconds during which the electrode is made cathodic and the potential attained, while the third column gives the number of seconds required for the potential to reach -0.13 volt during anodic polarization, i.e. the time required to complete the sulphate layer.

Table 7 .

Expt.	Cathodic		Anodic
	time	final potential	time to -0.13 volt
1	? secs.	very negative	70 secs.
2	53 "	-0.47 volt	41 "
3	40 "	-0.47 "	38 "
4	38 "	-0.47 "	38 "
5	34 "	-0.47 "	31 "
6	120 "	-1.23 "	76 "
7	52 "	-1.23 "	55 "
8	18 mins.	very negative	78 "

The greatest amount of sulphate formed corresponds to 507 millicoulombs. The electrode used in the above experiment had an apparent area of 1 $cm.^2$ and although no information regarding its effective area was available it could not have been more than 10 $cm.^2$ The above quantity of electricity would then be sufficient to oxidise and reduce a layer of $PbSO_4$, 16 molecules thick.

In the last series of experiments, the sulphate layer was always completed before the electrode was made cathodic. In the next series the electrode was made cathodic to potentials sufficiently negative to reduce the whole of the sulphate, i.e. only pure lead existed on the electrode. The electrode was now made anodic for increasing periods of time along the transition stage $Pb \rightarrow Pb^{++}$ and then made cathodic. The results are shown in table 8., where the second column gives the times of anodic polarization in each experiment and the third column gives the total time of anodic treatment up tp each experiment. In the fourth column are the times required to reach -0.53 volt. The polarizing current was the same for both anodic and cathodic, 1.o2 milliamps. (see next page).

Table 8.

Expt.	time of anodic in experiment	total time	time of cathodic to -0.53 volt
1	20 secs.	20 secs.	- secs.
2	20 "	40 "	- "
3	40 "	80 "	- "
4	40 "	120 "	1 "
5	40 "	160 "	2 "
6	40 "	200 "	3 "
7	40 "	240 "	3 "
8	40 "	280 "	3 "
9	40 "	320 "	3 "
10	80 "	400 "	7 "
11	120 "	520 "	10 "
12	130 "	650 " potential reached is -0.13 volt	200 "
13	200 "		260 "

In an experiment, immediately preceeding those in the above series, 700 seconds were required to form the complete $PbSO_4$ layer on anodic polarization. From table 8 it is seen that no increase in the quantities in the last column is observed until experiment 12. The total time of anodic polarization up to and including this experiment is 650 seconds and the potential reached is -0.13 volt, i.e. the $PbSO_4$ layer has been completed at this point. Although only 200 seconds of polarization takes place in

experiment 13, this quantity is sufficient to counter-balance that removed during the cathodic process in experiment 12.

When the electrode has been made cathodic until all the sulphate has been removed, and allowed to stand in the electrolyte the potential very soon reaches a steady value of -0.28 volt. If, however, the electrolyte is allowed to stand for a day or two so that the electrolyte becomes saturated with air the potential finally reaches a much lower value, ca. 0.0 volt. The same result is achieved in a few minutes if the electrolyte is stirred with a stream of oxygen gas. (On now making the electrode cathodic) a considerable amount of depolarization takes place before the hydrogen potential is attained.

Discussion.

When a lead electrode is anodically polarized in sulphuric acid it is initially very inert, its potential falling rapidly to the oxygen overvoltage passing through a slight maximum at about +2.20 volt (depending on the polarizing current density) and finally attaining a steady value of +1.85 volt. At this potential oxygen is liberated and lead peroxide formed, the latter soon covering the electrode with a dark brown film. During cathodic polarization, two depolarization processes occur. The first at +1.45 volt corresponds to the reduction of the peroxide to lead sulphate, and the second to the reduction of lead sulphate to metallic lead at -0.30 volt. When the initial quantity of peroxide on the electrode is small, both these reductions are quantitative, however, when a visible film of peroxide is present on the electrode surface, only a part of the peroxide is removed at +1.45 volt, the remainder being reduced by the hydrogen liberated at more negative potentials. This is also true of the reduction of the sulphate, and is due to the thickness of the films preventing electrochemical interchange between the metal and outer layers of the films.

When an electrode has been alternately oxidised and reduced for some time, the surface atoms of lead

become very active and are easily oxidised to sulphate. Eventually this active layer becomes fairly thick (it can be seen on the electrode as a slime). Finally when it reaches a certain thickness the reaction between metallic lead and lead sulphate no longer takes place reversibly and to completion. The deviations from this behaviour during the transition from $PbSO_4$ to Pb are,

(1) the time required to reach an arbitrarily chosen potential on the cathodic curve is not equal to the time of anodic polarization.

(2) No reduction of $PbSO_4$ takes place until the whole of the sulphate film, which can possibly be formed, is formed.

The above phenomena can be explained by the physical nature of the surface of such an activated electrode. A lead sulphate film is known to be highly protective, i.e. it covers the surface completely and protects the underlying metal from further corrosion and moreover it is a very poor conductor of electricity. The passivity of a fresh lead anode in sulphuric acid is due to this protective coating. However an activated electrode as used in the above experiments presents an entirely different system. It may be represented pictorially as in fig. 9 below. The film (a)-(b) of finely divided lead will be porous

and will therefore contain adsorbed sulphate ion. When such an electrode is made anodic, the outer metal atoms in the active layer will pass into solution as ions and be immediately precipitated as $PbSO_4$. This will continue until the sulphate layer is built up from (b) to (a).

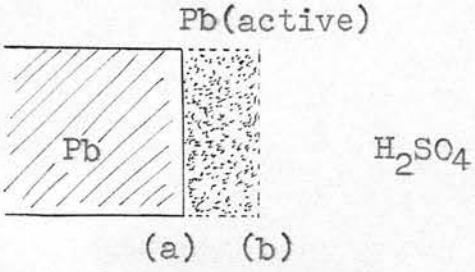


Fig. 9.

Owing to the poor electrical conductivity of a $PbSO_4$ film the only electrochemical reaction taking place must be at the surface of the bulk metal i.e. at (a). Then no cathodic reduction of sulphate to lead can take place until the sulphate film is completed; the series of experiments tabulated in table 8 support this view-point. Moreover, even when the complete sulphate film exists at the electrode, unless the film is very thin, only a part can be removed at the reversible potential, namely the few molecular layers nearest the bulk lead. This is shown in experiments 1, 6 and 8, table 7 where the electrode must be made cathodic to -1.23 volt before all the sulphate is reduced.

It is obvious that the active lead existing at such an electrode surface is capable of undergoing

ordinary corrosion in sulphuric acid. In hydrogen and nitrogen saturated solutions the finely divided lead is quite inert, but in air and oxygen saturated solutions corrosion rapidly takes place. It is possible that the large amounts of depolarization tabulated under β in table 6 is due to the rate of corrosion being comparable with that of electrochemical reduction of lead sulphate to lead.

Summary

(A) (1) The anodic and cathodic behaviour of nickel in N/5 sodium hydroxide has been studied (p.63).

(2) A fresh nickel electrode is inert in this solution owing to the presence of an air-adsorbed oxide film NiO, which is only removed at very negative potentials.

(3) At high positive potentials this is oxidised to Ni_2O_3.

(4) This oxide is reduced to NiO during cathodic polarization at E_h=-0.60 volt.

(5) A hysteresis effect similar to that studied in the earlier work is observed here.

(6) The anodic and cathodic behaviour of iron in N/5 sodium hydroxide has been studied (p.71).

(7) Iron is quite inert in this solution but adsorbs a considerable amount of hydrogen during cathodic polarization. This is subsequently removed when the electrode is made anodic.

(B) (1) The electrochemical behaviour of lead in M/10 sulphuric acid has been studied (p.82).

(2) Initially a lead electrode is very inert rapidly attaining high positive potentials

with the subsequent formation of lead peroxide.

(3) After lead peroxide has been formed two depolarization processes occur during a cathodic polarization (p.83).

(a) The first occurring at +1.45 volt is due to reduction of lead peroxide to lead sulphate.

(b) The second occurring at -0.30 volt is due to reduction of lead sulphate to metallic lead (p.84).

(c) These two electrochemical reductions are not quantitative (p.85), owing to the appreciable thickness of the solid films and to the poor electrical conductivity of the lead sulphate.

(4) The alternate oxidation and reduction leaves a surface film of lead on the electrode, which is very active passing into solution with great ease.

(5) This activity becomes very marked after some time, when oxygen dissolved in the electrolyte is able to bring the lead into solution as lead sulphate by an ordinary corrosion process (p.90).

(6) The process , lead $\rightleftharpoons$ lead sulphate should be quantitatively reversible, and was studied in greater detail. It was found that:

(a) The amount of lead which went into solution anodically as plumbous ion was equal to the amount which had previously been deposited during the cathodic polarization (p.86).

(b) Reverse did not hold true, that is, the quantity of electricity required to reach some arbitrary potential during the cathodic polarization was not equal to the amount of electricity passed during the anodic solution of lead (p.88).

(c). The above phenomena have been explained by a theory based on the appreciable thickness of the active layer of lead at the surface of the electrode

In conclusion, I wish to express my thanks to Dr. J.A.V. Butler for his deep interest in the work, for his kindly criticisms, and for his many valuable suggestions.

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